THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Improved toughness of adhesives filled with cork micro particles

By

Ana Sofia Oliveira Queirós Ferreira Barbosa

U.PORTO

FEUP FACULDADE DE ENGENHARIA
UNIVERSIDADE DO PORTO

Supervisor:

Lucas Filipe Martins da Silva

Co-Supervisor:

Andreas Öchsner

DEMec, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

February 2017

Departamento de Engenharia Mecânica

Faculdade de Engenharia da Universidade do Porto

Rua Dr. Roberto Frias

4200-465 Porto

Portugal

Abstract

Polymeric structural adhesives are an emerging joining method, increasingly selected in detriment to traditional joining techniques (welding, screws, rivets, braze welding and other mechanical joints). The aeronautical industry was the largest driving force of this technique, but nowadays adhesive joints can be applied in several sectors such as aerospace, automotive, nautical, construction, electronics, or even in traditional applications such as footwear.

Epoxy resins are one of the structural adhesives with greater applicability, mainly due to their versatility and mechanical, thermal and chemical resistance. The properties of this material derive mainly from its microstructure, which consists in an amorphous polymerized state heavily cross-linked, known as thermosets. Epoxies offer great strength and modulus of elasticity, low creep and good thermal resistance. However, due to the high crosslinking, the polymeric structure presents low toughness and a low resistance to crack initiation and propagation. There are three main methods documented in the literature to tackle this issue: polymer with phase separation, polymer without phase separation or the inclusion of a second (organic or inorganic). Natural raw materials can be used to promote toughness in brittle adhesives and currently different industries are encouraged to include these materials, with the aim to reduce the carbon footprint.

One solution, that has never been studied up to the beginning of this investigation, is the use microparticles of cork to enhance the toughness of brittle adhesives. Cork is an organic material with unique properties, obtained by a truly sustainable process, since it is renewable and biodegradable. Cork is characterized by being lightweight, flexible, substantially impermeable to liquids and gases, with excellent thermal, acoustic and vibration insulation, and is an innocuous and rootless material. Cork can be defined by an aggregation of sealed prismatic cells that work together. Thus, the structural properties of cork can be quite attractive to the reinforcement of brittle adhesives, particularly for improving the toughness, since the cork closed cells can absorb impacts quite easily. The main characteristics of cork result from the interaction between the

cells as a whole (plank, board or agglomerate). However, it was observed that most of the cork properties can also be observed in particles with smaller dimensions. It is intended that the cork particles create obstacles to the propagation of cracks, increasing the toughness of the adhesive. Apart from being a viable technique, this technology also allows to use a product (micro cork particles) ignored by the cork industry, which has a major importance in the Portuguese economy. Currently new applications are beginning to emerge for microcork particles, but most are usually burned. A new application for this material would represent for the cork industry a more sustainable application of these cork particles and a new perspective of potential economic gains.

It was necessary to perform a detailed evaluation of this new modified adhesive (resin / cork) since the final properties of the composite material depend not only on the properties of the resin and cork, but also the interaction between them. Thus, it is essential to ensure a uniform distribution of cork particles in the polymeric matrix and a good wettability of the particles by the resin. These two points were carefully studied. Cork is a very lightweight material which may lead to poor distribution of the cork and has in its composition waxes and other constituents which may cause poor wetting of the particles by the resin.

Several mechanical tests were performed to determine the material basic properties and then choose the best combination of amount/size/surface treatment of cork particles to incorporate in the resin. Bulk specimens of adhesive/cork were used to perform tensile, glass transition temperature (T_g) and fracture tests single edge notched bend (SENB). Single lap joints (SLJs) were also performed to evaluate the reinforced adhesive behaviour in a joint. In parallel to mechanical testing, thermal analysis differential scanning calorimetry (DSC) was also performed to evaluate the influence of the cork adhesive in the curing degree and Fourier transform infrared spectroscopy analysis (FTIR) to assess the chemical interaction between the resin and cork.

Structural adhesives are susceptible to environmental degradation, particularly in the presence of water and temperature, which can lead to a significant loss of properties. This concern is increased when natural particles are incorporated in the matrix, since most of these materials are responsible for a faster degradation of the composite

material. Thus, a mechanical and chemical analysis of the adhesive reinforced with cork micro particles were performed considering a hygrothermal aging.

With this research, it is concluded that the cork particles can be used to increase the toughness of brittle adhesives, without compromising the final properties of the modified adhesive.

Resumo

A colagem com adesivos estruturais poliméricos é um método de ligação emergente, cada vez mais selecionado em detrimento das técnicas de ligação consideradas tradicionais (soldadura, parafusos, rebites, brasagem e outras ligações mecânicas). A indústria aeronáutica foi a maior impulsionadora desta técnica, porém nos dias de hoje, a ligação de componentes por adesão já pode ser aplicada em vários sectores como aerospacial, automóvel, náutica, construção civil, eletrónica ou mesmo em aplicações mais tradicionais como o calçado.

As resinas de epóxido são um dos adesivos estruturais com maior aplicabilidade, devido à sua versatilidade e resistência mecânica, térmica e química. As propriedades deste material advêm principalmente da sua microestrutura sendo que no estado polimerizado são materiais amorfos e fortemente reticulados, denominando-se, portanto, por termoendurecíveis. As resinas epóxido possuem uma elevada resistência mecânica, módulo de elasticidade, baixa fluência e boa resistência térmica. Porém, devido à elevada reticulação da sua estrutura polimérica, possuem também baixa tenacidade, com uma fraca resistência à iniciação e propagação de fendas. Existem três principais métodos documentados na literatura para menorizar esta questão: utilização de um polímero com separação de fase, polímero sem separação de fase ou a inclusão de uma segunda fase (orgânica ou inorgânica). Materiais de origem natural podem ser usados para promover a tenacidade em adesivos frágeis e atualmente os diferentes sectores industriais são incentivados para incluírem na produção materiais de origem natural, de modo a diminuir a pegada de carbono.

Uma solução que nunca foi estudada até ao início desta investigação, é a utilização de micropartículas de cortiça para melhorar a tenacidade de adesivos frágeis. A cortiça é um material biológico com propriedades únicas, obtida por um processo realmente sustentável, uma vez que é renovável e biodegradável. A cortiça é caracterizada por ser leve, elástica, substancialmente impermeável aos líquidos e gases, excelente isolante térmico, acústico e à vibração, e é um material inócuo e imputrescível. A cortiça possui um conjunto de células prismáticas fechadas que funcionam em conjunto. Deste modo, as propriedades estruturais da cortiça podem ser bastante aliciantes para o reforço de

adesivos frágeis, especialmente para melhorar a tenacidade, uma vez que as células fechadas da cortiça podem absorver o impacto com bastante facilidade. As principais características da cortiça resultam da interação entre as células num todo (prancha, placa ou aglomerado), no entanto observa-se que a maioria das propriedades da cortiça podem também ser observadas em partículas de menores dimensões. Pretende-se que as partículas de cortiça criem obstáculos à propagação das fendas, aumentando a tenacidade do adesivo. Para além de ser uma técnica viável, esta tecnologia permite também usar um produto (micro partículas de cortiça) subaproveitado pela indústria corticeira, que tem um importante peso na economia portuguesa. Atualmente já começam a surgir novas aplicações para as micro partículas de cortiça, porém a maioria é geralmente queimado. Uma nova aplicação para este material representaria para a indústria corticeira uma aplicação mais sustentável das micro partículas e uma nova perspetiva de aplicação com potenciais ganhos económicos.

Foi necessário fazer uma avaliação cuidada do novo adesivo (resina/cortiça), uma vez que as propriedades finais deste material compósito não dependem somente das propriedades da resina e da cortiça, mas também da interação entre ambos. Deste modo é necessário garantir uma distribuição uniforme das partículas de cortiça na matriz polimérica e uma boa molhabilidade das partículas por parte da resina. Estes dois pontos foram alvos de um estudo cuidado. A cortiça é um material bastante leve o que pode conduzir a uma má distribuição da cortiça e possui na sua composição ceras e outros constituintes que podem originar uma má molhabilidade das partículas por parte da resina.

Foram feitos vários ensaios mecânicos para determinar as propriedades básicas dos materiais e assim selecionar qual seria a melhor combinação de quantidade/tamanho/tratamento superficial para adicionar à matriz de resina. Recorrendo a provetes maciços de adesivo/cortiça, foram ensaiados provetes de tração, foi determinada a temperatura de transição vítrea (T_g) e foram realizados testes de fratura *single edge notched bend* (SENB) para determinar a determinar a sua tenacidade. Foram ainda fabricadas juntas de sobreposição simples (SLJs) para avaliar o comportamento do adesivo reforçado com cortiça em junta. Paralelamente aos ensaios mecânicos, foi também feita uma análise térmica *differential scanning calorimetry* (DSC)

para avaliar a influência da cortiça no grau de cura do adesivo e uma análise espectrométrica *Fourier transform infrared spectroscopy* (FTIR) para aferir a interação química entre a resina e a cortiça. Os adesivos estruturais são sujeitos a degradação pelo meio ambiente, especialmente pela presença de água e temperatura, que pode conduzir a uma perda significativa das suas propriedades. Esta preocupação é acrescida quando se incorpora na sua matriz partículas de origem natural, uma vez que a maioria das fibras/partículas com esta origem são responsáveis por uma degradação mais acelerada do material compósito. Deste modo, foi feita uma análise das propriedades mecânicas/químicas quando o adesivo reforçado com micropartículas de cortiça é sujeito a um ambiente com humidade.

Com este estudo conclui-se que as partículas de cortiça podem ser utilizadas para aumentar a tenacidade de adesivos frágeis, sem que haja comprometimento das propriedades finais do adesivo por parte das partículas de cortiça incorporadas.

Acknowledgements

It takes a village to raise a child.

I can certainly make the same analogy for my PhD. It would be impossible to do all this work without support. Those that I will enumerate had a key role, one way or another, for this work to come to an end.

First, I would like to express my sincere appreciation to the supervisor of this thesis, Professor Lucas da Silva, which gave me the opportunity to start this long journey and kept pushing me forward with his constant support and academic inspiration. Thank you for always thinking that I am capable of doing better.

The extraordinary support provided by Professor Juana Abenojar and Juan Carlos del Real must also be acknowledged, who not only made their laboratory available for conducting my research but were also kind and generous to invite me to collaborate with them. I know that I always have the doors open in Madrid.

I would like to thank the warm support also given by the many colleagues of Adhesive Group and INEGI/IDMEC that accompanied me during this endeavour and eventually became true friends.

I would also want to refer those who work in the laboratories and workshops of FEUP and that helped me immensely through my work. Among them are Prof. Miguel Figueiredo, Prof. António Mendes Lopes, Eng. Rui Silva, Emília Soares, José Almeida, Albino Calisto, Eng. Cláudia Lopes.

I recognize that this research would not have been possible without the financial assistance, so the financial support by Foundation for Science and Technology (PTDC/EME-TME/098752/2008 and SFRH / BD / 88173 / 2012) are greatly acknowledged.

Last but not the least; I would like to thanks my family and friends for accepting nothing less than excellence from me. For the constant encouragement, motivation and support, without which I would never be able to achieve this goal. And most of all for my loving, supportive, encouraging, and patient Rui, whose faithful support, living every single

minute of it, and without whom, I would not have had the courage to embark on this journey in the first place.

Contents

List of Publications

1. A.Q. Barbosa, A. Q., L.F.M da Silva, A. Öchsner, J. Abenojar, J.C. del Real, Influence of the size and amount of cork particles on the impact toughness of a structural adhesive, The Journal of Adhesion, 88(4-6) (2012): 452-470.

2. A.Q. Barbosa, L.F.M da Silva, A. Öchsner, Effect of the amount of cork particles on the strength and glass transition temperature of a structural adhesive. Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials Design and Applications, (2013) doi: 1464420713493581

3. A.Q. Barbosa, A. Q., L.F.M da Silva, A. Öchsner, J. Abenojar, J.C. del Real, Utilização de micro partículas de cortiça como material de reforço em adesivos estruturais frágeis. Ciência & Tecnologia dos Materiais, (2013): 25(1), 42-49.

4. J. Abenojar, A.Q. Barbosa, Y. Ballesteros, J.C. del Real, L.F.M. da Silva, M.A. Martínez, Effect of surface treatments on natural cork: surface energy, adhesion, and acoustic insulation. Wood science and technology, (2014): 48(1), 207-224

5. A.Q. Barbosa, L.F.M da Silva, J. Abenojar, J.C. del Real, R.M. Paiva, A. Öchsner, Kinetic analysis and characterization of an epoxy/cork adhesive. Thermochimica Acta, 604 (2015), 52-60.

6. A.Q. Barbosa, L.F.M da Silva, A. Öchsner, Hygrothermal aging of an adhesive reinforced with microparticles of cork. Journal of Adhesion Science and Technology, 29(16) (2015): 1714-1732.

7. A.Q. Barbosa, L.F.M. da Silva, J. Abenojar, M. Figueiredo, A. Öchsner, A. Tensile Strength of a Brittle Epoxy Resin Reinforced with Micro Cork Particles: Effect of Size, Amount and Surface Treatment. Microscopy and Microanalysis, (2015): 21(S5), 9-10

8. A.Q. Barbosa, L. F. M. da Silva, M. D. Banea, A. Öchsner, Methods to increase the toughness of structural adhesives with micro particles: an overview with focus on cork particles, Materialwissenschaft und Werkstofftechnik 47.4 (2016): 307-325.

9. A.Q. Barbosa, L.F.M da Silva, A. Öchsner, J. Abenojar, Toughness of a brittle epoxy resin reinforced with micro cork particles: effect of size, amount and surface treatment Journal: Composites Part B (2016) http://dx.doi.org/10.1016/j.compositesb.2016.10.072

10. A.Q. Barbosa, L.F.M. da Silva, A. Öchsner, EAS Marques, J. Abenojar, Micro cork particles as adhesive reinforcement material for brittle resins, in: Advanced Structured Materials, ISSN: 1869-8433, in press

11. T.A.F. Rodrigues, F.J.P. Chaves, L.F.M. da Silva , M. Costa, A.Q. Barbosa, Determination of the fracture envelope of an adhesive joint as a function moisture, Materialwissenschaft und Werkstofftechnik, submited

Summary of thesis

1 Introduction

1.1 Background and motivation

Adhesive bonding is increasingly being used for joining materials, mainly due to its adaptability and ability to reliably join a large range of materials [1, 2]. Numerous industrial sectors have been progressively applying more adhesives, from cutting edge applications with large mechanical loads and requirements (i.e. aeronautical, aerospace, automotive and electronic), to more conventional uses (i.e. packaging and construction) [3-6]. Epoxy resins are the most commonly used structural adhesives, mainly due to their good mechanical, thermal and chemical properties, offering great strength, stiffness, toughness, durability and chemical resistance [7]. Epoxy resins are monomeric or oligomeric compounds containing two or more epoxy rings that may be opened catalytically or stoichiometrically, by reaction with multifunctional amines or carboxylic acids, generating a cross-linked network. When epoxies are in the polymerized state, they are amorphous and highly reticulated due to their thermoset nature [7]. The properties resulting from this microstructure are suitable for structural engineering applications, such as high strength and modulus of elasticity, low creep and good thermal strength [1]. However, the epoxy microstructure also presents some disadvantages, causing brittleness, with a low resistance to crack initiation and propagation [3, 4]. Hence, the scientific community has extensively studied processes for reinforcing epoxy resins, with more than forty years of research focusing on the improvement of the toughness of these thermosets [5, 8-10]. Several published works describe solutions to improve the toughness of brittle adhesives, such as the addition of a second polymer with a good toughness [11], the use of woven or knitted reinforcement [12], the inclusion of micro or nano inorganic (silicates, glass, alumina, etc.) [13] or organic particles [14]. In addition, natural materials can be used as reinforcement materials (i.e. cork or wood fibres) [14-18].

1.2 Problem definition

This thesis aims to both improve the fracture toughness of brittle epoxies and to find an alternative use for the unused cork powder.

The solution proposed covers both these problems as the reinforcement of the epoxy resins is made by the application of cork powder. This natural material presents excellent impact energy absorption, as well as good thermal and acoustic isolation properties. The cork particles should act as obstacles to the propagation of the cracks thus increasing the toughness of the adhesive.

In addition of being seemingly technically possible, this technique would also allow the use of a product (cork powder) that is currently not exploited by the cork industry and which has an important impact in the Portuguese economy. Cork powder is normally burnt, leading to unnecessary energy consumption and frequent accidents. The successful use of this material for reinforcing epoxies would open a completely new market for the cork industry, with many potential benefits.

1.3 Objectives

The main objective of this research work is to investigate the application of cork micro particles as a reinforcement material for brittle adhesives.

The specific objectives are listed below:

- to characterize the cork micro particles in terms of size, shape and surface energy;
- to determine the intrinsic mechanical properties of the selected adhesive;
- to define the best combination between cork and adhesive, i.e., size amount and surface treatment of cork particles to improve adhesive toughness;
- to evaluate the chemical/physical interactions between the cork and adhesive that may affect the curing process;
- to evaluate the hygrothermal behaviour of the adhesive reinforced with cork particles.

1.4 Research methodology

In order to achieve the objectives of this PhD thesis, the following methodology was adopted:

- In the past decades, several new methods to increase the toughness of structural adhesives were developed. Hence, a ***literature review*** of the methods used to increase the toughness of structural adhesives with micro particles was performed in **Paper 1**. This article presents an overview of the main methods to toughen adhesives, with a special focus on cork particles.
- A preliminary assessment of the mechanical properties of the adhesive reinforced with micro particles of cork was carried out in **Paper 2**. ***Impact toughness tests*** were selected as a tool to evaluate the influence of size, amount and surface treatment of cork particles, since the specimens' production and the results analysis is relatively simple.
- The initial results show that the specimens with 1% cork, a size of 125-250 μm without surface treatment present the best results. To have a better understanding of this effect, ***tensile tests*** were carried out to evaluate the influence of the cork amount (0, 0.5, 1, 2 and 5%) on the basic adhesive properties in **Paper 3**. The influence of the cork amount was also assessed by ***glass transition temperature*** measurements. By combining the results of these two tests, it was possible to draw some conclusions about the influence of the amount of cork on the ductility of the adhesive.
- Knowing that the amount of cork present in the adhesive influences the mechanical properties, an evaluation of its influence on the cure reaction was performed in **Paper 4**. **Differential scanning calorimetry *(DSC)*** and **Fourier transform infrared spectroscopy** (***FTIR)*** tests were performed to understand if the improved mechanical properties of the cork reinforced adhesive resulted solely from a mechanical interaction or if there was any type of chemical reaction between the adhesive and the cork particles.
- ***Fracture tests*** of bulk adhesive specimens were performed to fully understand the influence of size, amount and surface treatment of micro particles of cork on the fracture toughness of the reinforced adhesive in **Paper 5**. A ***Taguchi design***

of experiments was used to quantify the influence of each parameter under study and the interaction between them.

- An analysis of the effect of moisture and temperature on the degradation of an adhesive reinforced with micro cork particles was undertaken in **Paper 6**. The ***coefficient of moisture diffusion*** and effect of water exposure on the ***tensile tests*** and ***glass transition temperature*** was also investigated.

1.5 Outline of this thesis

This thesis consists of six appended papers and a summary.

Paper 1 - A. Q. Barbosa, L. F. M. da Silva, M. D. Banea, A. Öchsner, **Methods to increase the toughness of structural adhesives with micro particles: an overview with focus on cork particles,** *Materialwissenschaft und Werkstofftechnik* 47.4 (2016): 307-325.

Abstract of paper 1

Structural adhesives are used increasingly in new applications replacing conventional joining methods. Epoxy adhesives have the widest range of application of the various classes of adhesives arising principally from their extremely wide set of performance properties. They are known for their high stiffness and strength, as well for their low ductility and toughness. Currently, there is an increasing interest in developing methods of improving toughness. A toughened adhesive in general contains elastic or thermoplastic domains dispersed in discrete form throughout the resin matrix, in order to increase the resistance to crack-growth initiation. This paper provides an overview of the current developments in the use of reinforcement materials and introduces the reader to early findings on the use of micro particles for toughness enhancement of adhesives. The theme of the use of materials of natural origin as reinforcement materials, giving special emphasis to the use of cork particles as toughener material is also presented.

Paper 2 - A.Q. Barbosa, A. Q., L.F.M da Silva, A. Öchsner, J. Abenojar, J.C. del Real, J. **Influence of the size and amount of cork particles on the impact toughness of a structural adhesive,** The Journal of Adhesion, 88(4-6) (2012): 452-470.

Abstract of paper 2

The inclusion of particles (nano or micro) is a method to improve the mechanical properties, such as toughness, of structural adhesives. Structural adhesives are known for their high strength and stiffness but also for their low ductility and toughness. There are many processes described in the literature to increase the toughness, one of the most common being the use of rubber particles. In the present study, natural micro particles of cork were used with the objective to increase the impact resistance of a brittle epoxy adhesive. The idea is for the cork particles to act like crack stoppers and absorb impact leading to higher absorption of energy. The influence of the cork particle size and amount were studied. Particles of cork ranging from 38 to 250 mm were mixed in the epoxy adhesive Araldite 2020® from Huntsman. The amount of cork in the adhesive was varied between 1 and 5% by weight. Surface treatment (low pressure plasma) was applied to the cork powder to assess the effect of the interaction adhesive-cork with several degrees of adhesion. This evaluation was made using impact tests and it was evident that impact absorption was related to the size and amount of cork particles in the resin, considering a uniform particle distribution.

Paper 3 - A.Q. Barbosa, L.F.M da Silva, A. Öchsner, **Effect of the amount of cork particles on the strength and glass transition temperature of a structural adhesive**. Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials Design and Applications, 228 (4) (2014) 323-333

Abstract of paper 3

The inclusion of particles (micro or nano) is a method to improve the mechanical properties, such as toughness, of structural adhesives. Structural adhesives are known

for their high strength and stiffness but also for their low ductility and toughness. There are many processes described in the literature to increase the toughness, the use of rubber particles being one of the most common processes. In the present study, natural micro particles of cork were used with the objective to increase the ductility of a brittle epoxy adhesive. The idea is for the cork particles to act like a crack stopper. The influence of the amount of cork particles was studied. Particles of cork ranging in size from 125 to 250 mm were mixed in the epoxy adhesive Araldite 2020® from Huntsman. The amount of cork in the adhesive was varied between 0.5% and 5% in weight. This evaluation was made using tensile tests and it was evident that the failure strain was related to the amount of cork particles in the resin. The results concerning the single lap joints and the glass transition temperature confirm the increased ductility obtained in the tensile tests.

Paper 4 - A.Q. Barbosa, L.F.M da Silva, J. Abenojar, J.C. del Real, R.M. Paiva, A. Öchsner, **Kinetic analysis and characterization of an epoxy/cork adhesive**. Thermochimica Acta, 604 (2015), 52-60.

Abstract of paper 4

Epoxy resins are the most common structural adhesives due to their good mechanical, thermal and chemical properties. However, the structure of these thermoset polymers, due to the high crosslinking, also causes brittleness, with a low resistance to the initiation of cracks and their propagation. The inclusion of particles (nano or micro) is a common method to improve the mechanical properties such as toughness of structural adhesives. In the present study, natural micro particles of cork were used to increase the toughness of a brittle epoxy adhesive. The main objective of this research was to investigate the effect of the amount of cork particles in the cure reaction of a brittle epoxy, knowing that the amount present influences the mechanical properties. This study was developed using specimens with 0.5, 1, 2 and 5% (volume) of cork and without cork, as reinforcement material of a brittle resin. In general, the cork particles do not influence the curing process, although they slightly change the curing mechanism. Also,

cork particles decrease the glass transition temperature (T_g) and have a plasticizer effect in the epoxy resin.

Paper 5 - A.Q. Barbosa, A. Q., L.F.M da Silva, A. Öchsner, J. Abenojar, **Toughness of a brittle epoxy resin reinforced with micro cork particles: effect of size, amount and surface treatment** Journal: Composites Part B – http://dx.doi.org/10.1016/j.compositesb.2016.10.072

Abstract of paper 5

Structural adhesives are increasingly being used for new applications, replacing conventional bonding methods. Epoxy resins are the most common structural adhesives used due to their suitable mechanical, thermal and chemical properties, as well for their low ductility and low toughness. Several researchers, have in the past decades, found it necessary to reverse these properties and find new ways to increase the toughness of these adhesives. There are many processes depicted in the literature on how to increase the toughness of brittle adhesives, the use of rubber particles being one of the most common. The inclusion of particles (nano or micro) is a successful method to improve toughness of structural adhesives. In the present study, natural micro particles of cork are used with the objective of increasing the toughness of a brittle epoxy adhesive. The concept is for the cork particles to act like as a crack stopper leading to more energy absorption. The influence of the cork particle size, amount and the presence of a surface treatment were studied. Cork particles ranging from 38-53 and 125-250 µm were mixed into adhesive Araldite 2020®. The amount of cork in the adhesive varied between 0.25 to 1% in volume. The toughness of the adhesive was assessed through fracture tests, using three-point bending specimens. A Taguchi design experiments was used to understand the influence of each parameter under study (amount, size and presence of surface treatment) and the interaction between them. With this research it was possible to conclude that cork can improve toughness and cork amount, size and the use of plasma surface treatment have influence on the mechanical properties.

Paper 6 - A.Q. Barbosa, L.F.M da Silva, A. Öchsner, **Hygrothermal aging of an adhesive reinforced with microparticles of cork**. Journal of Adhesion Science and Technology, 29(16) (2015): 1714-1732.

Abstract of paper 6

In the present study, natural micro particles of cork are used with the objective to increase the toughness of a brittle epoxy adhesive. The cork particles act as a crack stopper, leading to more energy absorption. This fact occurs because cork presents a remarkable combination of properties (low density, low cost and sustainability of the raw material). Adhesives are susceptible to the presence of moisture in the environment. There are several studies that refer that moisture can degrade the molecular structure of the adhesive, and, therefore, its mechanical properties. The main objective of this research is to investigate the effect of moisture on the degradation of an adhesive reinforced with micro cork particles, knowing that cork presents a great capability to absorb water. The water absorption and desorption characteristics have been studied, for specimens without cork and with 1% cork, 125–250 μm. The moisture uptake behaviour in the adhesive was studied to obtain the coefficient of moisture diffusion. The effect of water exposure on the mechanical properties and glass transition temperature was also investigated. It was observed that the presence of water alters the mechanical properties of the adhesive (with and without cork), but these changes are not permanent.

2 Adhesive and cork particles

2.1 Epoxy adhesive – Araldite2020®

The selected adhesive was Araldite 2020®, from Huntsman Advanced Materials (Pamplona, Spain). This adhesive consists of two components (100/30 by weight), and it is characterized by having low viscosity (150 mPa.s). It is a transparent epoxy adhesive which cures at 100 °C in 15 min. Component A, the epoxy resin, is composed by diglycidyl ether of bisphenol A, (DGEBA) and diglyciddyl ether of 1,4-butanediol (DGEBOH). On the other hand, component B (hardener) is composed by isophorone diamine (IPDA), as schematically represented in Figure 1. Araldite 2020® was selected mainly because it is a very brittle adhesive, in which any increase in toughness can be easily observed. Since this adhesive is transparent and slightly viscous, the observation (with naked eye) of the cork particle distribution can also be easily performed. Each specimen was visually inspected before testing to ensure that the particle distribution was randomly uniform and there were no voids or other defects.

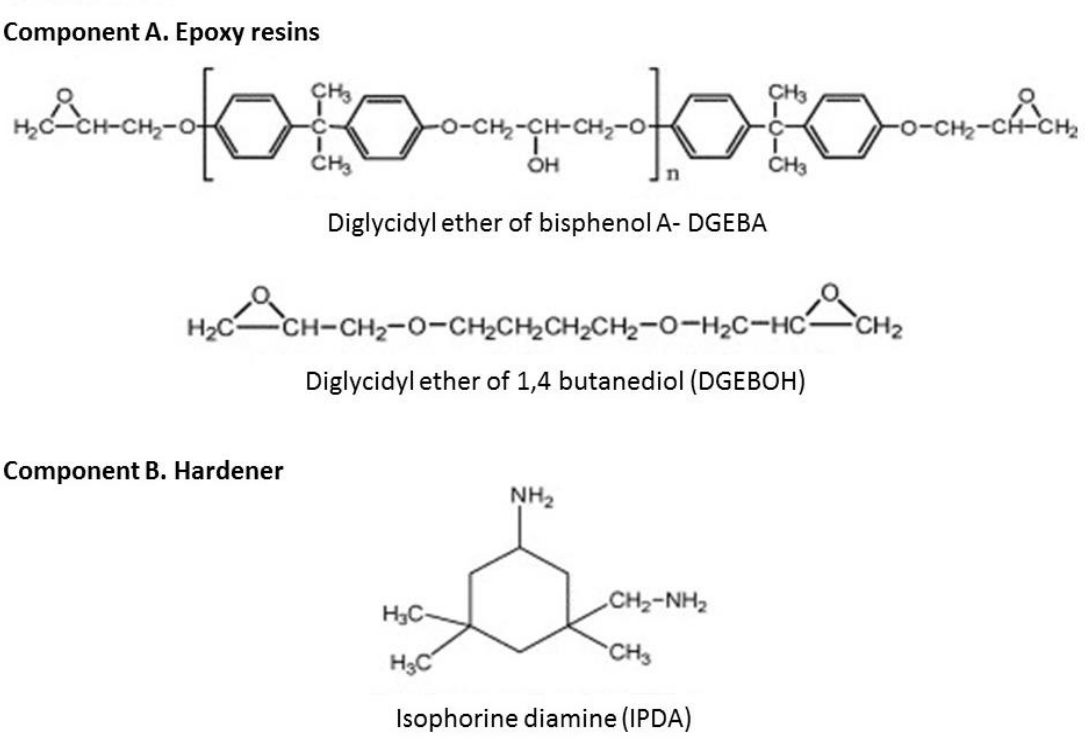

Figure 1 - Molecular structure of Araldite 2020® components.

2.2 Micro particle of cork

Cork is defined as being the external layer of the cork oak (Quercus suber L.) stem and branches. It is a biological material notable for having several unique properties [19-22]. This specie stands out from the oaks family essentially for the bulky peel of woven bark (cork). Cork is the main product of cork oak exploration and is considered to be a truly sustainable product, since it is renewable and biodegradable. Cork harvesting is an environmentally friendly process as not a single tree needs to be cut down, and after being removed, the bark renews itself before the next harvesting.

In order to accurately characterize cork, macro and microscopic properties have to be considered, since both are rather remarkable and suitable for many engineering applications. Macroscopically, cork is light, elastic and considerably impermeable to liquid and gas. It is a thermal and electric insulator as well an acoustic and vibration insulation absorber. It is also innocuous and unaffected by microbial activity, with the ability to be compressed without lateral expansion. Microscopically, cork is constituted by layers of dead cells arranged in a honeycomb shape. The cell membranes have a certain degree of sealing, and are filled with a gas similar to air, which occupies about 90 % by volume. The combination of the honeycomb shape and the closed cell membranes is what provides the cork with its characteristics [23, 24]. Cork wall cells are basically constituted by suberin, lignin, and cellulose.

Although initially limited, the interest on the understanding of the properties of cork increased significantly with the industrialization of the bottle stopper production process. While stoppers are the most widespread and perhaps the oldest application of cork, nowadays there is a noteworthy interest in expanding the use of this material. During the production process of stoppers, a large amount of cork considered unsuitable is not used and discarded during production. This material is often granulated and used in a variety of applications, being mainly employed for the production of cork/rubber composites [20]. This material is used in several products such as: automobiles, airplanes, joints for electric and gas equipment, acoustic and vibration insulators, products for cleaning of oil spills, footwear, among several others applications [25, 26].

Cork is a closed cell material with prismatic cells that work together and elastically orthotropic axisymmetric relative to the direction of the tree. This type of structure is of

particular interest, as it can be used to reinforce a brittle adhesive, particularly to improve its toughness. In addition, the closed cells can also efficiently absorb impacts. Nevertheless, the properties of an adhesive/cork composite are not only dependent on the material properties, but also on the interfacial adhesion properties between the cork and the resin, size and amount of cork particles and mixing conditions [27].

Cork can be used in several shapes of varied dimensions, namely as plates, granules or particles with a few microns. In this research, two distinct sizes of micro particles were used, within different range sizes: 38-53 and 125-250 µm (see Figure 2). Smaller particles present a damaged honeycomb cell structure, with some open cells and where most particles are composed only by one cell. In contrast, bigger particles present a honeycomb cell structure with several adjoined cells, containing few open cells in the edges and closed cells in the particle core.

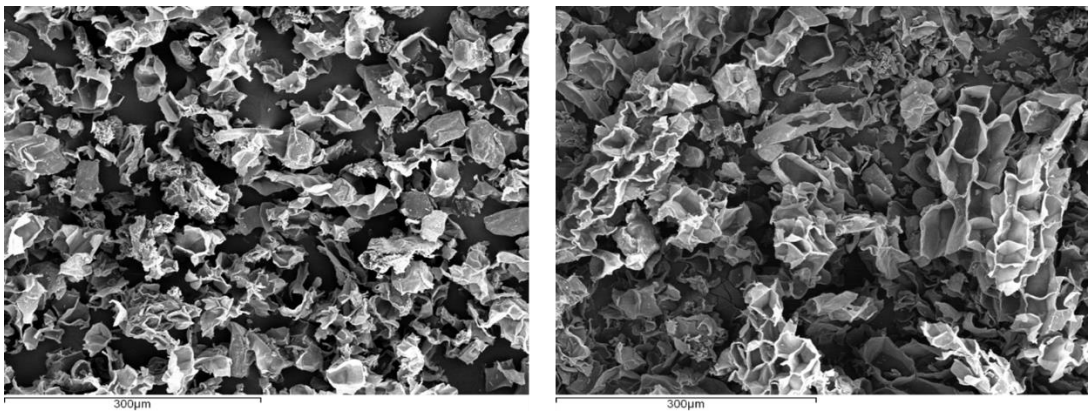

Figure 2 - Micro particle of cork; left - 38-53 µm size; right 125-250 µm size.

The process of adhesion between the epoxy resin and the cork particles may be dependent on physical (mechanical interlocking) and chemical bonds. Cork particles are inherently porous and have open cells which can be filled by the epoxy resin to achieve a mechanical interlocking effect.

The interface between the cork particles and the resin is a key factor in the toughening process, as it is essential to guarantee that loads can be effectively transferred between the particles and the matrix. Hence, it is crucial to have good wetting between the resin and the cork particles, so that a strong bond can be assured. When good adhesion is

achieved, the reinforcing particles act as crack stoppers and not as defects in the resin matrix, with the applied stress being successfully transferred to the particles from the matrix [28]. It is known that weak bonds between particles and the matrix lead to lower fracture toughness when compared to strongly bonded particles.

As the particle chemistry controls both the rate of wetting and the strength of interaction with polymers, these features can be regarded as even more important than the bulk properties. Therefore, to guarantee suitable interfacial interactions, the surface properties of a particle must occasionally be modified accordingly to their chemistry. Some degree of modification or treatment is often suggested for application on all surfaces prior to adhesive bonding. There are several techniques that can be used to modify the reinforcement's materials surface (particularly those derived from natural sources) such as: graft copolymerization of monomers onto the surface, the use of maleic anhydride copolymers, alkyl succinic anhydride, stearic acid, etc. Likewise, plasma treatments are also beneficial to treat polymeric surfaces [29, 30].

When cork is used as a reinforcement material, it is essential be aware that this material is hydrophobic due to the presence of suberin (one of its main components) and that this behaviour can decrease the level of adhesion between the cork and the resin. It is also important to consider that cork is a heterogeneous natural material that shows visible changes according to the board's origin and even the direction of cork growth.

Some modifications can be implemented on the cork surface in order to increase wettability, for instance: atmospheric pressure plasma torch (APPT), low-pressure plasma chamber (LPPC) or silanization [30]. It is imperative to ensure that this type of treatment only modifies the cork surface properties without altering its bulk properties. These treatments act by creating reactive chemical groups on the cork's surface, which allow the resin to chemically bond with the cork cells.

Using atmospheric plasma treatment, the contact angle between the cork surface and the water drop decreases. Plasma treatment is able to change the cork behaviour from hydrophobic to hydrophilic, independently of cell growth orientation (radial, tangential or axial). This ensures that the adhesion properties of the cork particles are uniform throughout its surface.

However, it is necessary to take into account that, when analysing the surfaces that have been treated with plasma, some important differences are observed in comparison to the particles that were not treated. The cell wall thickness of the treated particles is thinner than that of the particles that did not have surface treatment, suggesting that the plasma treatment is responsible for the erosion of the cell walls.

2.3 Manufacture of the adhesive reinforced with cork micro particles

The step that precedes any of the tests performed is the production of adhesive reinforced with micro cork particles. It is a crucial stage which depends on the adhesive properties. A homogeneous mixture of cork micro particles in the adhesive must be guaranteed in order to avoid the introduction of air bubbles and ensure uniform distribution of particles. The cork and the adhesive were mixed using a centrifugal mixing machine, SpeedMixer DAC 150TM (Hauschild, Hamm, Germany), during 90 seconds at 1500 rpm. Initially, cork was mixed with the resin and the hardener was added later to the mixture. This procedure was the same for the different sizes and amounts of the cork. However, after mixing at room temperature, a sufficiently uniform distribution of the cork particles could not be reached due to the low density of the cork particles and the low viscosity of the adhesive. To ensure better particle distribution after mixing, the adhesive/cork mixture was heated to 50°C for 10 min to increase the adhesive viscosity. After this procedure, the adhesive/cork mixture was mixed again in the centrifugal mixing machine, creating a uniform and random particle distribution.

Commonly, bulk specimens are manufactured by pouring or injecting the adhesive in a mold with the final shape or by applying pressure between plates. Due to the brittle behaviour of Araldite 2020® adhesive, the second method was selected. This technique is described in the French standard NF T 76-142, an is able to produce plate specimens without porosity and with a high level of quality. Figure 3 shows schematically the working principle of this technique, which consists in pouring adhesive into the central part of the mold. The volume of adhesive poured must be larger (approximately 5%) than the volume inside of the cavity defined by a silicone rubber frame. This ensures that no voids appear. The thickness of the silicone rubber frame defines the final

thickness of the adhesive plate and seals the adhesive very tightly, enabling the application of hydrostatic pressure to the adhesive. The plates are cured under high pressure and temperature in a hot plate press. According to the datasheet, this adhesive can cure within a temperature range between room temperature and 100°C. As the cork has a very low density the highest temperature was selected, so that the curing process would be as fast as possible, avoiding the agglomeration of cork particles in one part of the plate. Due to the combination of heat and pressure the surface finish of the plate is excellent. This is crucial, since the mechanical properties are dependent of the presence of defects such as voids, microcracks and non-uniform particle distribution [31, 32].

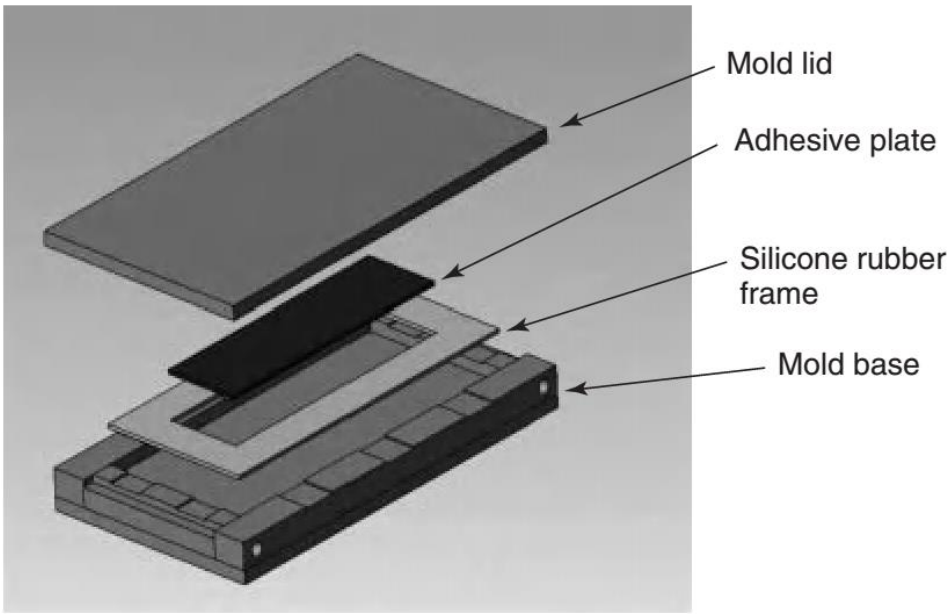

Figure 1 - Mold for bulk specimens according to NF T 76-142 standard, expanded view with steel plates and silicone rubber

In situ tests are one of the most reliable method to characterize adhesives and adhesive joints. The Single lap joint (SLJ) is one of the most commonly used joint configuration, being easy to manufacture and cheap to produce [32]. To aid in the manufacture of this type of specimens an annealed carbon steel mold was used, see Figure 4. The mold ensures that the substrates' alignment is correct, restricts their movement, controls the overlap length and defines the adhesive thickness, due to its specially designed alignment pins, shims and positioner blocks. To ensure easy release of the specimens after manufacture, a mould release agent was applied to all surfaces of the mold. [31].

Before bonding, the substrates surface was carefully prepared, removing dust, oils or oxides with sandblasting, followed by an acetone degreasing. The curing process was the same that was applied to the bulk specimens. After the curing process, the specimens were carefully removed from the mold, separated with a saw and the excess adhesive on the side of the joint was removed with a file. The specimens were manufactured individually in a mold and the adhesive thickness was controlled by the use of appropriately sized packing shims. High strength steel adherends were used to avoid yielding of the adherends. The adherend selected was a high strength steel (DIN C65 heat treated) with a yield strength of 1260 MPa.

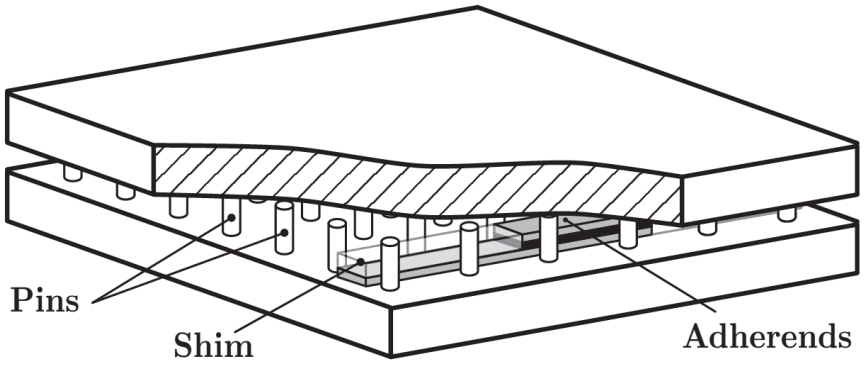

Figure 2 – Carbon steel mold used for SLJ [31].

3 Test methods

The use of a correct experimental methodology is crucial task for the evaluation of a new adhesive. A complete analysis of the adhesive reinforced with cork must be achieved through different material characterization techniques, in order to properly understand how the size, amount and surface treatment of cork particles can influence the adhesive properties. These experimental tests can be divided in the following main groups:

- Evaluation of the necessity to modify the surface of cork (**Paper 2 and 5**);
- Measurement of the failure strength of the adhesive reinforced with cork (**Papers 2, 3, 4, 5 and 6**); tests on bulk and *in situ* specimens;

- Evaluation of the thermal properties of the adhesive (**Papers 2, 4 and 6**);
- Analysis of the main functional groups of the adhesive (**Papers 4 and 6**)
- Assessment of the durability of the adhesive reinforced with cork (**Paper 6**).

All the experimental tests performed are described in the following sections. The majority of the tests are standardized (ASTM, ISO or BS), which provides a basis for defining the test parameters.

3.1 Particle size analysis

Particle size analysis was a very important step for understanding how the size of the cork particles is distributed in the samples tested. Initially this evaluation was made using a scanning electron microscope (SEM), analysing just the size and geometry of the cork particles. This method was used in **Papers 1, 2, 3, 5** and **6**. To analyse particle size distribution a Malvern Mastersizer 2000 apparatus (Malvern, United Kingdom) was used. The particle size data obtained with this analysis complemented the results obtained in SEM analysis. Three tests were made for each condition. This method was used in **Paper 5**.

3.2 Density measurement

The knowledge of the particle density is essential for this study, as this information is fundamental to determine the amount of cork to be added to the epoxy resin. The density of treated and untreated cork particles was measured using a helium pycnometer, with the reference Micromeritics AccuPyc 1330 (DataPhysics, Neurtek Instruments, Eibar, Spain). The density of the impact test specimens was calculated using the Archimedes principle. This technique was applied in **Paper 1**.

3.3 Contact angle

As mentioned above, to achieve a strong bond it is crucial to have good wetting between resin and the particles. In this research work, plasma treatment was used to alter the

cork's particle surface, and consequently to increase its wettability. Contact angle measurements were then used to study changes in surface energy that happen after plasma surface treatment. Contact angle measurements can be related to surface tensions or energies using Young's equation [43]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} cos\theta \quad \text{(equation 1)}$$

where θ is the measured contact angle (°) and γ is the surface energy and the subscripts *SV* stands solid-vapour, *SL* for solid-liquid, and *LV* for, liquid-vapour. Depending on the model used, an expression for γ_{SL} can be combined with Young's equation resulting in a relation between the contact angle and the liquid's surface tension. The solids surface energy can then be calculated by the Owens-Wendt-Rabel-Kaelble (OWRK) method. The OWRK method distinguishes between polar and dispersive fractions of the surface energy and uses a geometric mean of these in the expression for γ_{SL} [43]. The wettability of materials was evaluated using a OCA 15 goniometer (DataPhysics, Neurtek Instruments, Eibar, Spain). To evaluate the contact angle, the samples were placed in a chamber (25°C) with vapour of the liquid used in the measurement. The liquids used were distilled water (polar liquids), and diiodomethane (nonpolar liquids). The use of these liquids allowed a complete determination of the cork's surface energy. This technique was applied in **Paper 1**.

3.4 Failure strength tests

Failure strength tests are commonly used to determine the tensile stress-strain curve of bulk specimens [32]. This test was selected because the stress-strain curve can be used to determine the tensile strength, failure strain and Young's modulus. These mechanical properties are intrinsic to the material, being obtained under a uniform and uniaxial stress state, without influence of the adherends [32]. Tensile test dogbone-shaped specimens according to BS 2782 standard [34] were manufactured, produced from bulk adhesive plates cured in a steel mould [35]. Figure 5 shows the dimensions of the machined specimens, with a thickness of 2 mm. The tensile tests were carried out in an Instron 3367 universal test machine with a capacity of 30 kN (Norwood, USA). This test was performed at room temperature under a constant crosshead rate of 1 mm/min. The

strain was measured with an extensometer (Instron Norwood, USA). Three specimens were tested for each condition. This experimental test procedure was applied in **Papers 2, 3, 4, 5 and 6**.

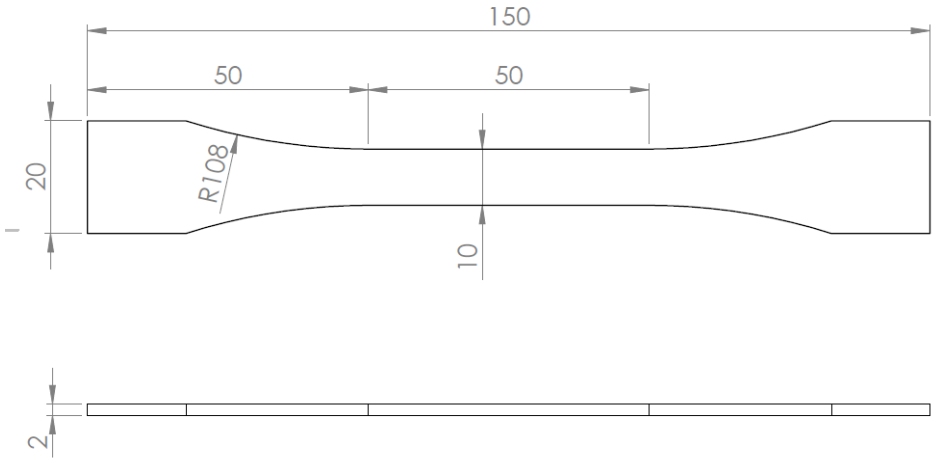

Figure 5 - Dog-bone tensile test specimens according to BS 2782 standard (dimensions in mm).

3.5 Single lap joints (SLJ)

SLJs specimens are usually used for gathering mechanical information of adhesively bonded systems such as the shear strength. This test was selected since the specimens rather simple to manufacture and resemble the geometry of many practical applications [31]. The SLJ tests were carried out in an Instron 3367 universal test machine with a capacity of 30 kN (Norwood, USA) at room temperature and test speed of 1 mm/min. Three specimens were tested for each condition. The geometry and dimensions of the SLJs are provided in Figure 6. The SLJ test is standardized in ASTM D1002-99 and also ISO 4587:2003 [39, 40]. The maximum loads were extracted from the experimental load-displacement curves.

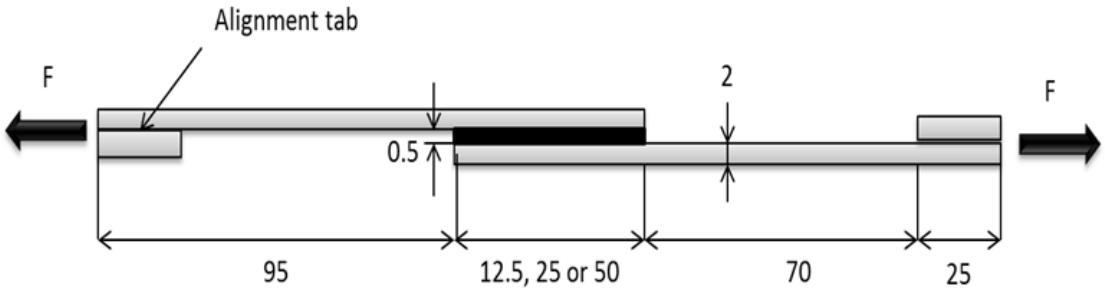

Figure 6 - Single lap joints geometry according to ASTM D 1002 (dimensions in mm).

It is known that for ductile adhesives, the SLJ strength is proportional to the overlap. Therefore, joints of increasing overlap (12.5, 25 and 50 mm) were tested to check the adhesive ductility. This experimental test and its results are described in **Paper 3**.

3.6 Toughness impact tests

Toughness impact tests were used to conduct the initial study of the bulk adhesive properties, since they are quite easy to perform, giving a very clear idea of the cork's influence on the reinforced adhesive. These tests also follow the applicable standards for polymeric materials. Figure 7 shows the dimensions of the machined specimens, manufactured according to ASTM E23-02a [33]. The toughness impact tests were performed in a Rosand V1.01 machine (Rosand Precision, Ltd., Stourbridge, UK), an instrumented falling weight impact test machine. This test was executed with a mass of 4 kg (5 J of available energy), at room temperature and with an initial velocity of 1.57 m/s. Three specimens were tested for each condition. This experimental test and its results are described in **Paper 1**.

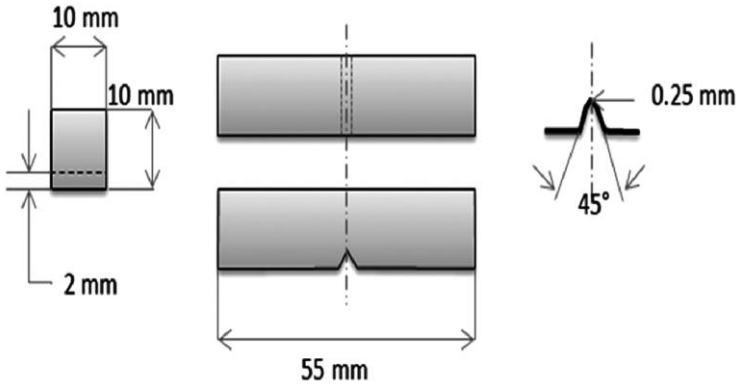

Figure 7 - Dimensions of Type A Charpy impact test specimens.

3.7 Fracture tests on bulk specimens

Fracture tests can be performed using the adhesive in bulk form and/or in adhesive joints. However, when bulk specimens are used, a more accurate determination of the adhesive properties can be achieved [32]. As the tested adhesive was very brittle, the application of fracture tests on adhesive-joint specimens was not possible. The cured plates were machined into single edge notched bend (SENB) specimens, again using standard techniques developed for polymers (ISO 2000) [36]. SENB specimens were used to determine the toughness of the epoxy in terms of the critical-stress-intensity factor, K_{Ic}, and the critical strain energy release rate, G_{Ic}, satisfying the requirements of ASTM D5045-14 and ASTM E 399 standards [37, 38]. SENB geometry consists of a centre-notched beam loaded in three-point bending (see Figure 8). The pre-crack (a) was introduced by lightly tapping a razor blade (0.3 mm) into the tip of the machined crack. In order to obtain precise K_{Ic} and G_{Ic} values, it is crucial to create a very sharp pre-crack and eliminate most residual stresses around the crack tip. The pre-crack length (a) ranged from about 5.4 to 6.6 mm. After opening the pre-crack, it was necessary to measure it with the greatest possible accuracy. For this purpose, a magnifying glass (Zeiss/Germany) was used in conjunction with an image capture software, Leica LAS 4.3 (Leica Microsystems/Germany).

The plane-strain fracture toughness tests were carried out in an Instron 3367 universal testing machine (Norwood, USA), with a capacity of 30 kN. This test was performed at room temperature with a crosshead speed of 10 mm/min to avoid the viscoelastic

behaviour of the epoxy. Five specimens were tested for each condition, as requested by the applicable standard. This experimental test was applied in **Paper 5**.

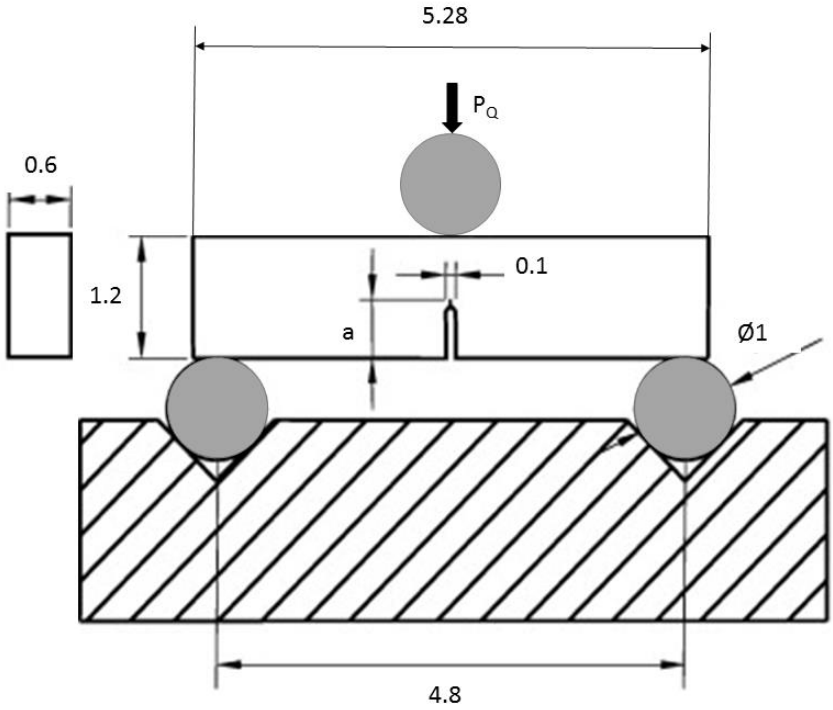

Figure 8 - Single edge notched bend (SENB) geometry specimen used for bulk adhesive fracture testing and test setup (dimensions in cm).

3.8 Measurement of glass transition temperature (T_g)

The glass-transition temperature (T_g) is the most important thermal property of a cured adhesive, being often not too far from room temperature or its service temperature. The determination of T_g is very important since it separates rubbery adhesives from rigid ones, and is something to be avoided in service. For epoxies, it is typically between 80 and 150 °C. T_g is related to the molecular position. Below T_g, adhesives have a glasslike behaviour, because the polymeric chains have much less mobility and the polymer is "frozen" over small timescales, hence, the stiffness and strength are high and the strain to failure is low. On the other hand, above T_g, adhesives have a rubberlike behaviour as the polymer chains move more freely [31, 32].

T_g can be measured by thermal analysis, dilatometry or mechanical damping. In this research, two different methods were used to measure T_g: dynamic mechanical analysis and differential scanning calorimetry. Since the heating rates in each of the methods are

different, the temperatures measured are also different. However, regardless of the method used, the same trend in the results was observed. These techniques were applied in **Papers 2, 3, 4 and 6.**

A dynamic mechanical analysis method which was initially proposed by Zhang et al. [41] was used to determine the T_g of the composite cork/resin. The method involves excitation of the test specimen during the heating and the cooling phases. T_g is measured by registering the damping of the specimen as a function of temperature. In this case, it is defined as the temperature at which the peak value of damping is observed. The heating rate should not be excessively high to ensure homogeneous temperature distribution in the specimen and avoid a post-cure of the adhesive. Figure 5 shows schematically the T_g measurement apparatus. The specimen used for this test consists of a pre-cured sheet of the polymer that is fastened between the beam and a constraining layer (see Figure 6).

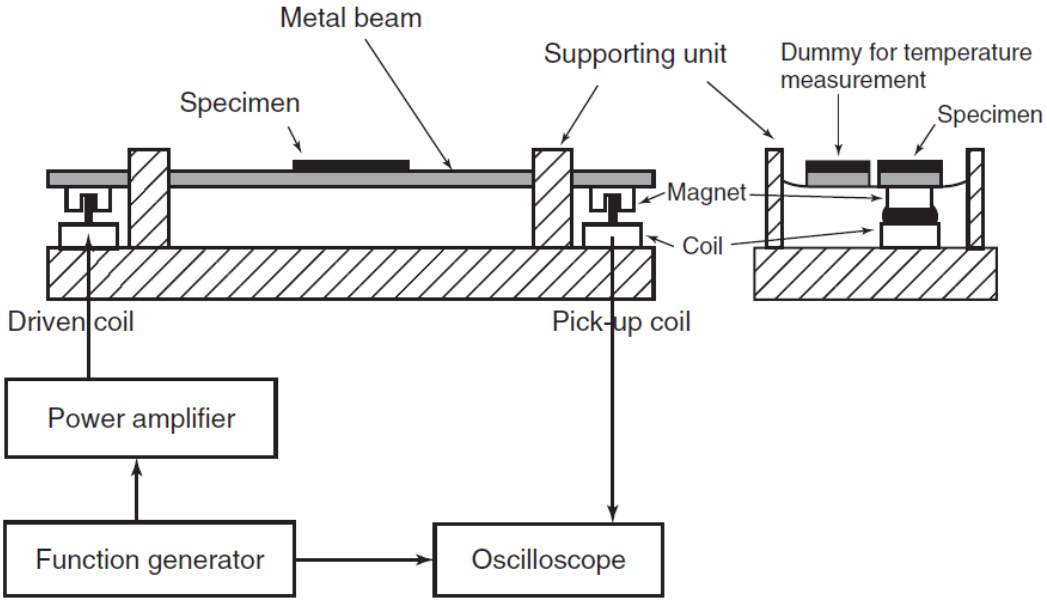

Figure 3- Schematic diagram of the apparatus used in the measurement of T_g.

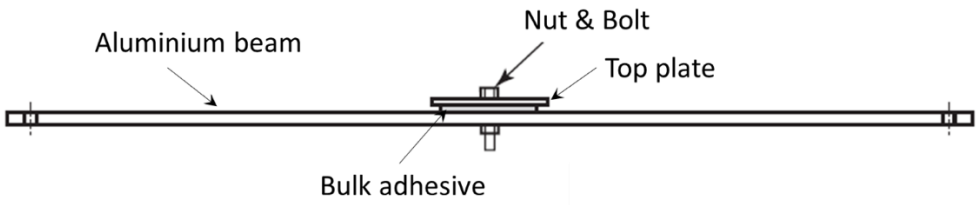

Figure 4 - Schematic representation of the bulk specimen for T_g measurement.

Differential Scanning Calometry (DSC) was also used to investigate T_g. DSC examines how the heat capacity of a material changes with temperature. With this method, a specimen of adhesive is heated or cooled at a constant rate, and any changes in heat capacity are recorded. T_g A Mettler Toledo GmbH T_g /DSC apparatus (Greifensee, Switzerland) was used to perform this analysis. A heat rate of 10 ^{o}C/min and 6 mg of adhesive with different amount of cork or neat epoxy resin were used, tested in temperatures ranging from -20 ^{o}C to 200 ^{o}C. Two tests were performed for each condition. Two scans were made on each material sample to determine the thermal history of the material. The midpoint in temperature was used to compare materials. A correlation between the mechanical properties and the thermal and chemical properties was made possible by the T_g measurements.

3.9 Fourier transforms infrared spectroscopy (FTIR)

FTIR can be very useful for adhesive research, since this is a highly sensitive and quick method to achieve a high quality spectrum. This technique can be used both in solid and liquid adhesives and allows the identification of organic and inorganic compounds. This material characterization technique was used in this research to study the influence of the amount of cork in the curing process and to the observe the main functional groups present after hygrothermal degradation. FTIR measurements were carried out by a PerkinElmer Spectrum Two apparatus (Waltham, USA). A wave length of (4000–600) cm^{-1} and 0.2 cm^{-1} of scanning velocity were used. These tests were carried out with a $LiTaO_3$ detector (15,700– 370 cm^{-1}) and a KBr window. Two tests were performed for each condition. The Spectrum 10 PerkinElmer software Spectrum (Waltham, USA) was used for data analysis. This technique was used to assess the effect of the cork amount

in the curing process and to evaluate the effect of the hydrothermal degradation in the cork reinforced adhesive. FTIR techniques were applied in **Papers 4 and 6**.

3.10 Differential Scanning Calometry (DSC)

DSC analysis examines how the heat capacity (C_p) of a material changes with temperature. DSC was used in this research to evaluate the effect of the amount of cork particles in the cure reaction and thermal properties of a brittle structural adhesive. This test is important to detect if, besides modifying the mechanical properties of the resin, the cork can also noticeably alter the crosslinking process and the curing mechanism. This technique was applied in **Paper 4.**

To analyse the cure kinetics of specimens with and without cork particles, a DSC machine supplied by Mettler Toledo GmbH (Greifensee, Switzerland) was used. Aluminium crucibles of 40 ml, with around 7.5 mg of the composite or neat resin for each test were used. Nitrogen acted as purge gas, at 80 ml/min. Isothermal tests of 30 min, at different temperatures (70, 85 and 100 °C) were chosen and a second segment of dynamic scanning from the isothermal temperature to 200 °C at a scan rate of 5 °C/min was added. This procedure made possible the calculation of the total heat of reaction. Two tests were performed for each condition. Non-isothermal (dynamic) tests were also carried out at different heating rates (5, 10 and 20 °C/min) from 0 to 200 °C.

3.11 Durability tests

It is well known that adhesives, like all polymers, are susceptible to the presence of moisture in the environment or when directly immersed in liquids. Water molecules can degrade the molecular structure of the adhesive and alter its mechanical properties. Polymers reinforced with natural fibres/particles are known to be severely affected by the presence of moisture, since the degradation occurs mainly in the resin-particle interface. Hence, it is imperative to understand the behaviour of these adhesives under adverse conditions, in order to predict their long-term performance.

For moisture diffusion studies, the bulk adhesive was machined into rectangular plates with dimensions of 60 mm x 60 mm and a thickness of 1.0 ± 0.1 mm. These dimensions ensure that diffusion is one dimensional [42]. Three specimens were prepared for these studies, one for each condition (neat resin and 1% cork). This technique was applied in **Paper 6**.

3.12 SEM

Scanning electron microscope (SEM) was extensively used during the course of this work, being employed to analyse the fracture surface in various types of tests, determine particle size and geometry, and to confirm if random particle distributions were successfully achieved. All this information was essential for correlating results. SEM analyses were carried out using a JEOL JSM 6301F/Oxford INCA Energy 350/Gatan Alto 2500 microscope (Tokyo, Japan). This method was applied in **Papers 1, 2, 3, 5,** and **6** of this research.

4 Conclusions

Despite varied and wide ranging objectives, this work can be understood as a thorough study on the application of cork particles as a reinforcement material for increasing the toughness of a brittle adhesive. The experimental methodology was devised to thoroughly characterize the cork particles, the adhesive and the cork reinforced adhesive. After the conclusion of this research work, some general conclusions could be drawn:

- The presence of cork was found to change the mechanical properties of the epoxy resin. By varying the size and volume of the particles and modifying the interface between cork and resin, the mechanical properties could be optimized.
- Micro cork particles were found to increase the toughness of brittle epoxy adhesives. The particle amount and size present noticeable influence on the adhesive toughness. Since cork particles do not have a uniform geometry, its

structure may diverge depending on biological and mechanical factors, which are particularly difficult to control.

- The surface treatments conventionally used to treat reinforcement particles were not effective in cork particles. Low-density plasma treatment decreased the contact angle and increased the wettability of cork. There was an erosion of the surface which increased roughness, promoting adhesion between cork and the adhesive. However, this treatment is also responsible for an erosion of cell walls, leading to a decrease in cell wall thickness, resulting lower mechanical performance. Furthermore, with this erosion, resin can penetrates into the cork cell structure, which is not desirable for energy absorption.
- The curing processes of the neat resin and the resin reinforced with cork was found to be very similar. FTIR analysis demonstrated that curing of the adhesive leads to the formation of different functional groups of the resin and that the cork particles had no direct influence on the curing of the adhesive. This effect is probably due to the dimensions of the incorporated particles, which remain at the micro level not affecting the molecular structure of the adhesive.
- Considering hygrothermal degradation, the neat resin and the resin reinforced with cork were found to have very similar diffusion rates, since the presence of cork did not have a significant influence on the absorption/desorption of moisture. A deterioration of the mechanical properties was found to occur with the moisture uptake although it was also observed that the cork behaviour is not compromised by the presence of water. Cork is a rootless material, inherently resistant to moisture, while most natural fibres used to reinforce polymers are not and, therefore, susceptible to moisture degradation.
- As a final remark, it can be said that the use of micro cork particles as a reinforcing material can be an excellent application of a natural product, opening new and exciting development opportunities in this area and offering promising potential in the future.

5 Future work

In research projects with a significant experimental component such as this, work can never be considered as complete. As new information is obtained, new questions arise and it becomes evident that much work remains to be done in the field of cork reinforcement. Some suggestions for the continuity of this work follow:

- Firstly, it would be interesting to transpose this technology to other types of adhesives, observing the influence of adding cork to different adhesive chemistries. It would be necessary to perform a new cork amount/size optimization study for each selected adhesive. The Araldite 2020® is a low viscosity adhesive, making it very difficult to test this adhesive in adhesive-joints specimens. Most of the tests performed in this research were carried out in bulk form because of this limitation. Thus, it would be quite interesting to assess the effect of reinforcing an adhesive that would allow the tests in joints to be carried out
- A possible next step would consist in performing fracture toughness tests at high and low temperatures. These tests would be able to assess if the cork reinforcement alter the temperature dependence of the adhesive's fracture toughness.
- A complementary study on the influence of cork reinforcement on the fatigue behaviour of the adhesive would also provide valuable scientific data and enable the design of long lasting structures with these materials.

- Another promising adhesive joint configuration that might make use of this reinforced material is graded adhesive joints. As noted by the results, different amounts of cork lead to changes in the mechanical properties. Thus, by varying the amount of cork along the bondline, stress distributions in an adhesive joint could be modified to give improved mechanical properties.

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Literature review

Methods to increase the toughness of structural adhesives with micro particles: an overview with focus on cork particles

A.Q. Barbosa[1]*, L.F.M. da Silva[2], M. D. Banea[3], A. Öchsner[4]

[1] INEGI, Rua Dr. Roberto Frias 400, 4200-465, Porto, Portugal

[2] Department of Mechanical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

[3] Federal Center of Technological Education in Rio de Janeiro, Brazil

[4] Griffith School of Engineering, Griffith University (Gold Coast Campus), Building G39 Room 2.22, Parklands Drive, Southport Queensland 4214, Australia

ABSTRACT

Structural adhesives are increasingly being used in new applications replacing conventional joining methods. Epoxy adhesives have the widest range of application of the various classes of adhesives arising principally from their extremely wide set of performance properties. They are known for their high stiffness and strength, as well for their low ductility and toughness. Currently, there is an increasing interest in developing methods of improving toughness. A toughened adhesive in general contains elastic or thermoplastic domains dispersed in discrete form throughout the resin matrix, in order to increase the resistance to crack-growth initiation. This paper provides an overview of the current developments in the use of reinforcement materials and introduces the reader to early findings on the use of micro particles for toughness enhancement of adhesives. The theme of the use of materials of natural origin as reinforcement materials, giving special emphasis to the use of cork particles as toughener material is also presented.

Keywords: Toughness, adhesive, epoxy, micro-particles, cork

1 – Introduction

One of the most used technique for joining materials is adhesive bonding, mainly due to its versatility [1]. Adhesives can be used to join a large range of materials (i.e. metal, ceramics and polymers) and combinations of any of these materials [2, 3]. Thus adhesive joints have been increasing their application in various branches of industry, from applications with high mechanical stress and requirements (i.e. aerospace, aeronautic, electronic and automotive), to more traditional applications (i.e. packaging sport and construction) [3-8].

Epoxies are the most common structural adhesives due to their good mechanical, thermal and chemical properties. They offer greater strength, rigidity, toughness, durability and chemical resistance than polyesters, but at a higher price and with more difficulties in processing [9]. When epoxies are in polymerized state, they are amorphous and highly reticulated due to their thermoset nature. Epoxy resins are monomeric or oligomeric compounds containing two or more epoxide rings that may be opened catalytically, or stoichiometrically, by reaction with multifunctional amines or carboxylic acids, to give a cross-linked network [9]. This microstructure results in very useful properties for applications of structural engineering, such as high modulus of elasticity and strength, low creep, and good thermal strength [1, 10]. However, the structure of these thermoset polymers also causes brittleness, with a low resistance to the initiation of cracks and their propagation [4, 5]. For this reason, their toughening has been extensively studied in the last decades [4, 11-13]. There are some solutions available in literature to improve the toughness of brittle adhesives, such as: addition of a second polymer with a good toughness [14], use of woven or knitted reinforcement [8], inclusion of micro or nano inorganic (silicates, glass, alumina, etc.) [10] or organic particles[15]. Also, natural materials can be used as reinforcement materials (i.e. cork or wood fibres) [16-18].

This paper provides an overview of the recent developments in the use of reinforcement particles in the adhesive technology and summarizes the main methods used to obtain a reinforced material with micro particles. The main parameters that influence the particle performance (i.e. their nature and properties which depends on their size, interparticle distance, particle/matrix interaction and volume fraction) and how they

influence the toughness of the final composite/adhesive were discussed. Finally, the paper ends with some considerations about the application of cork microparticles as reinforcement material for adhesive joints.

2 – Toughness

2.1 - Concepts

In short words toughness can be defined as the resistance to fracture of the material when stressed, i.e., the ability of a material to absorb energy and plastically deform without fracturing. So, toughness requires a balance between strength and ductility [1, 14]. Traditionally, toughness has been defined as the ability of a material to dissipate deformation energy without crack propagation. It can be also defined by the ability of a material to rapidly distribute within itself both the stress and strain caused by a suddenly applied load.

Toughness is one of the factors that are believed to govern the strength of materials (amongst material's elastic properties and the size of the crack from which failure initiates). Therefore, it is important to have full knowledge of the material toughness to develop a reinforced adhesive [19]. The concept of fracture mechanics to develop new toughened materials considers the crack effect and defects in the strength and also that the fracture behaviour is governed by characteristics of viscoelasticity, shear yielding, and dilatational deformation involving cavitation [4, 5, 20].

2.2 – Methods to measure toughness

The evaluation of toughness of adhesives reinforced with micro particles can be made using fracture tests on bulk adhesive specimens and on adhesive-joint specimens. In these tests, linear elastic fracture mechanics approach is considered [21, 22]. Fracture mechanics assumes that the structure is not continuous, allowing presence of a second phase, manufacture defects or any other damage caused during its work life [23].

Bulk tests are an excellent approach to evaluate the mechanical properties of adhesives. In case of paste and liquid adhesives, bulk specimens are regularly formed by casting the adhesive into a mold and then curing the specimens according to the manufacturer's instructions [21]. Specimens can be obtained by plates and machined or casted with the final form, according to the standard dimensions (i.e. compact tension (CT) or single edge notched bend (SENB) (see Figure 1 a))). Also, test specimens to determine the fracture toughness (K_{Ic}), or fracture energy (G_{Ic}), using standard techniques developed for polymers (ISO 2000 or the equivalent ASTM D5045) can be used. SENB and CT geometries are recommended over other configurations because they have predominantly bending stress states which allow smaller specimens sizes to achieve plane strain [7, 24].

According to ASTM D5045[24], the property K_{Ic} (G_{Ic}) characterizes the resistance of a material to fracture in the presence of a sharp crack, under severe tensile constraint, in a neutral environment, such that the state of stress near the crack front is close to plane strain. It is also necessary that crack-tip plastic (or nonlinear viscoelastic) region to be small compared with the crack size and specimen dimensions in the constrain direction. A K_{IC} value is believed to represent a lower limit value of fracture toughness. This value may be used to estimate the relation between failure stress and defect size for a material in service wherein the conditions of high constrain described above would be expected. The K_{IC} (G_{IC}) value of a given material is a function of testing speed and temperature [7, 24]. Choosing between CT or SENB specimens is influenced by a few factors:

- Amount of material available, because CT specimens are larger than SENB specimens;
- Type of crack propagation observed: the tests are quasi-static and unstable crack initiation from the initial defect is intended in the test.

The manufacture of bulk specimens is not an easy task, as there are some requests that must be assured. For example, the presence of air bubbles must be minimized to obtain a complete filling of the mold and avoid uncontrolled exothermic degradation of the

adhesive during cure. In case the adhesive has a second phase, for example reinforcement material, a uniform distribution of the particles must be assured. Thus, in most cases it is preferable to test adhesive joints rather than bulk specimens.

The application of fracture tests on adhesive-joint specimens dates back to 1960 [25-27]. Fracture tests on adhesive-joints specimens, also known as in situ tests [21], represent a more realistic situation as adhesives in their common application are applied in a thin layer (0.1 to 2 mm thick), becoming part of a system formed by adherend, adhesive and the interface [7, 28]. Adhesive joint specimens present some advantages but also disadvantages compared to bulk specimen tests. For example, this test method is useful in the way that it can be used to develop design parameters for bonded assemblies. On the other hand, fracture tests on adhesive joints are generally more complex than tests on bulk adhesive specimens. Furthermore, due to the fact that the adhesive is present as a thin layer, it may be constrained by the presence of nearby substrates and the failure path may be influenced by the poor adhesion with the substrate.

Fracture tests on adhesive joints are commonly conducted in mode I (tensile opening mode), mode II (in-plane shear mode), and mixed mode I/II (combination of mode I and II), as shown in Figure 1 b). The key to success in all linear elastic fracture mechanics (LEFM) tests is to ensure that the substrates do not deform plastically during loading [7].

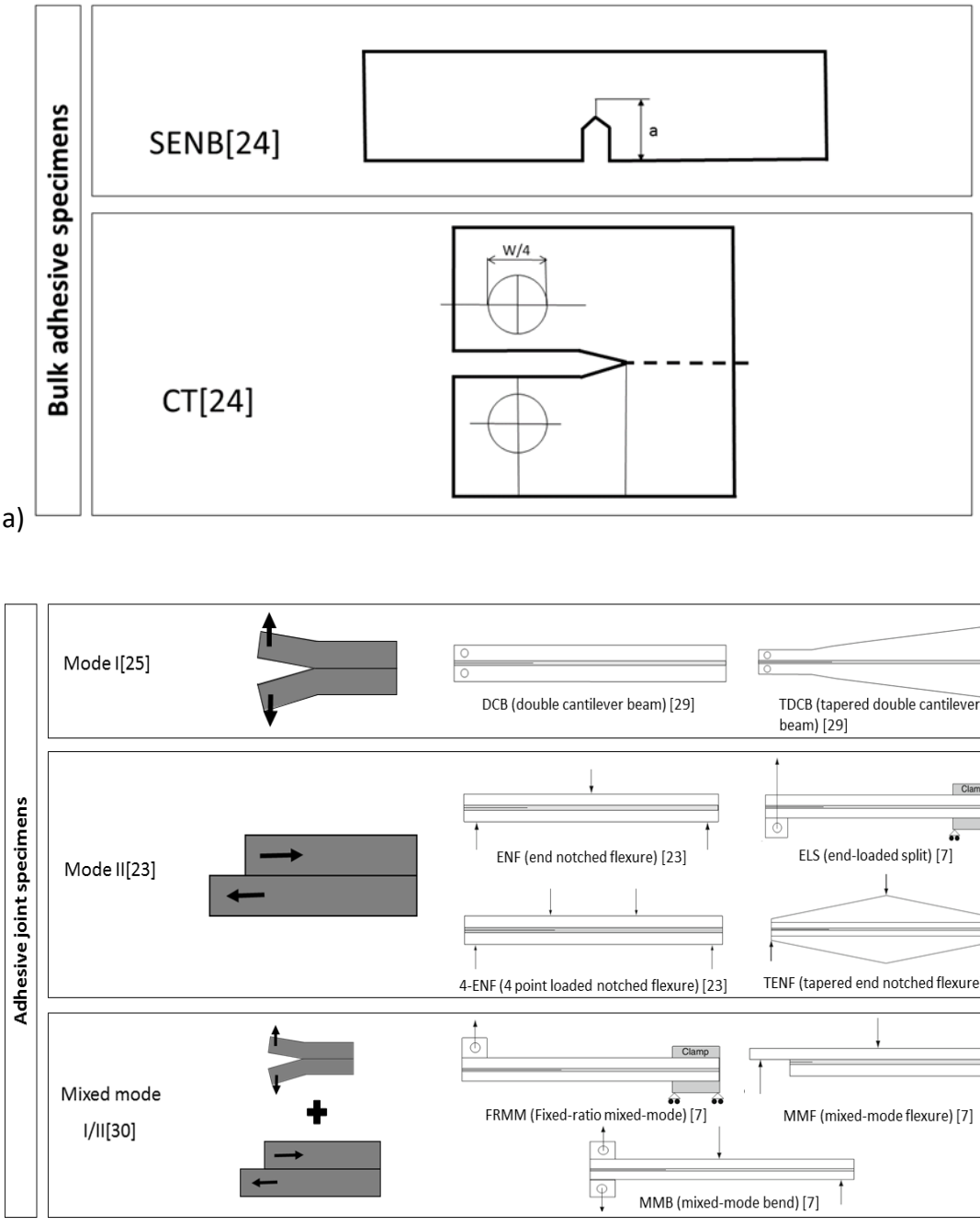


Figure 1 – Specimen geometry for bulk adhesive (a) and adhesive-joint specimens (b) [7, 23-27, 30-32].

3 – Toughened adhesives

Toughened structural adhesives represent a large area of scientific and technological concern. The issue of polymer toughening emerged in the 70's and since then has experienced a steady increase of interest all over the world [19, 33]. Though many aspects remain to be explained and many questions still wait for a definitive answer,

nowadays toughened adhesives hold a consistent and well defined position in the adhesive market [34]. The microstructure and properties of the polymers can be modified by covalent cross link, adjusting the molecular weight and degree of crystallinity. But also, greater changes can be achieve combining a polymer with other polymers or by adding ribs with particles or fibres to form composites. Figure 2 shows a schematic diagram of a toughened adhesive network. Toughening agents act like crosslink agents, i.e., mechanical properties can be changed.

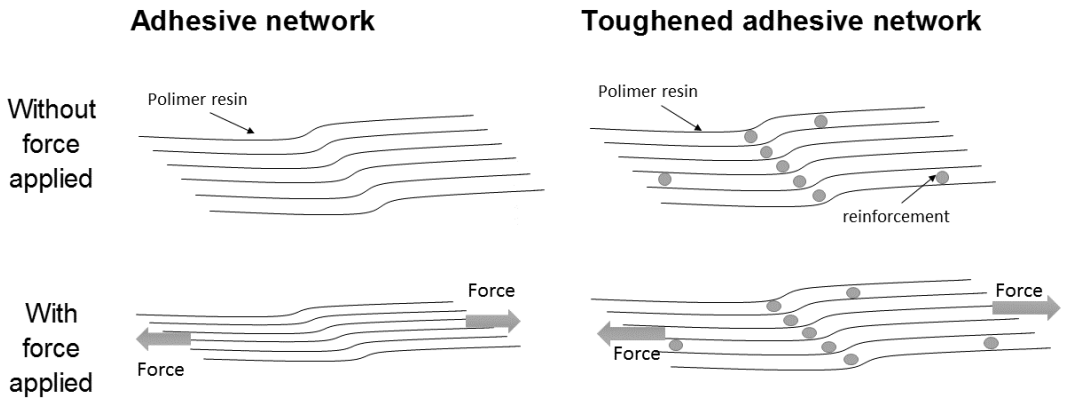


Figure 2 - Schematic diagram of adhesive network at shear strength test, adapted from [7].

Toughening by using a reinforcement material presents a few advantages. In general, it is more economically attractive, since to develop a new chemical formula for an adhesive is a long and costly process [34, 35]. However, the use of thermosetting materials is often limited by their toughness properties, which affect the durability of components and place strong constrains on design parameters. The main goal is to develop new tougheners which do not affect adhesives` thermo-mechanical properties and the ease of processing. Figure 3 illustrates the main methods used to increase the toughness of adhesives.

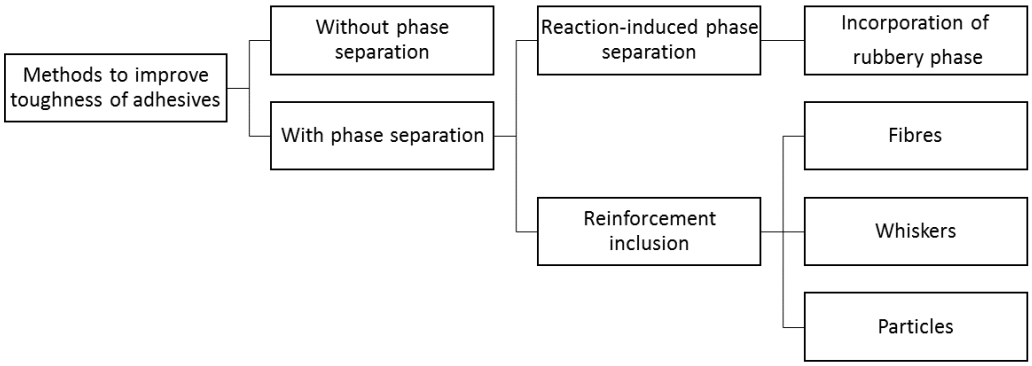


Figure 3 - Methods to improve the toughness of adhesives.

Two different methods to improve the toughness of adhesives have emerged, both with their own advantages and disadvantages:

- Polymer without phase separation, known as chemical modification of molecular structure [36];
- Polymer with phase separation, with a supramolecular organization [36, 37];

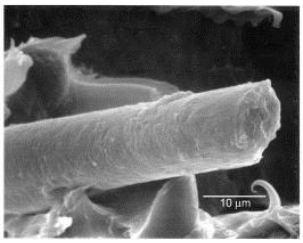
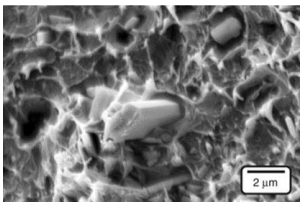
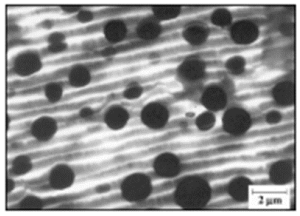
There are two main procedures to generate second-phase dispersion in a modified-thermosetting polymer:

- Phase separation during polymerization of an initial homogeneous solution (reaction-induced phase separation) [38-43];
- Dispersion of a second phase in the starting monomers (reinforcement inclusion) [44-47].

Improving toughness with a second phase dispersed has proven to be successful and can be used in a large range of plastics that nowadays are commercially available [34]. This approach can be used in polymers with great impact in the world economy such as: polyvinylchloride (PVC), polymethylmethacrylate (PMMA), polypropylene (PP), polycarbonate (PC), and most recently in thermosettings resins, such epoxies, polyimides and unsaturated polyesters [5, 34].

In general, toughened adhesives present satisfactory results when the second phase is homogeneously dispersed within the matrix and adequately bonded to the matrix [34]. The first time that a second phase material has been used as a reinforcing material was intended only to reduce production costs [48, 49]. However, currently its application goes beyond and can be used to change innumerable properties. Table 1 shows the main types of reinforcements for toughened materials.

Table 1 – Types of reinforcements for toughened materials [50-54].

Denomination	Shape	
Fibres	one very long axis with other two axes either often circular or near circular	
Whiskers	have a preferred shape but are small both in diameter and length as compared to fibers	
Particles	present very similar dimensions in the three axes, a form of short ‘‘fibers’’	

The reinforcement material is chosen depending on the final property which is desired for the composite/adhesive matrix. Usually, the toughness enhancement involves the addition of micron- or nano-sized soft (elastomeric or thermoplastic) or rigid (glass, ceramic or metal) particles into the resin matrix. These fillers are then expected to provide extrinsic toughening mechanisms [55]. Currently, there are various materials which are used as toughener promoters, such as liquid rubbers, spherical rubber

particles [56], core shell particles [45, 57], glass beads [58, 59] microvoids [60, 61], hyperbranched polymers [62] or combinations of these materials [63, 64].

In general, second phase inhomogeneities dispersed in a brittle matrix acts as obstacles impeding the moving crack front thereby increasing fracture toughness either by increasing the length of the crack front and/or by blunting the crack tip. Crack deflection, flexion, and crack tip blunting are very common phenomena in the presence of a second phase material in the vicinity of a propagating crack front causing reduction in stress intensity [65].

There are several types of materials that can be used to increase the toughness of adhesives. The choice of the most suitable material is based (or should be based) on sustainable product development, where, in addition to obtaining the best mechanical properties of the adhesive, are considered economic, ecological and social sustainability issues.

4 – Methods to increase the toughness of adhesives with micro particles

This section aims to provide the reader a thorough idea of the mechanisms inherent to the use of particles as reinforcement to increase the toughness of adhesives. The main advantages and disadvantages of using this method to increase the toughness are presented. Also, the main factors that influence the toughening mechanism are discussed, not forgetting that the final material is a composite material and should be studied as such.

The use of particles dispersed in epoxy resin systems serves two main purposes:

- To reduce the cost of a component by incorporating a high percentage of low-cost material;
- To provide the composite with some desired property [7, 66].

Doing a quick read through the main research done in this area easily follows that the majority of the particles used as reinforcing materials are nanoparticles, and

consequently, most of the scientific research directs to this field of research [67]. However, in this paper only micro particles are considered as reinforced materials.

Since the World War II, increasing the toughness of adhesives and the subsequent techniques are the subject of study by various researchers [7] [13, 68-73]. For most of the studied particles (rigid particles), the inclusion of micro fillers in general increase the adhesives strength, though toughness decreases since these fillers may induce stress concentrations, initiating cracks that could cause the adhesive failure [74]. Some authors [55] agree that the conventional approach of introducing micron-sized particles into the polymer matrix has failed to yield significant improvements in the fracture toughness of highly cross-linked thermosetting polymers.

Particulate fillers modify the physical and mechanical properties of polymers in many ways [20]. When a particle is added into a polymer matrix to form a composite, it plays an important role in the properties (mechanical, electric, thermal) of the composite [75]. The structure of thermosetting polymers, in general, and epoxy resins in particular, generally leads to one highly undesirable property in that they are relatively brittle materials, with a poor resistance to crack initiation and growth. Therefore, toughening of epoxies has become a necessity to ensure the feasibility of these materials for practical applications. Consequently, the addition of a second phase, either rigid or soft can be a solution to this problem by improving the fracture toughness of brittle epoxies. The mechanical behaviour of composite materials reflects the interactions between their various constituents [54].

The inclusion of particles in a resin matrix can bring to the composite several improvements, however, it can also modify the polymer structure. The principal ways, in which a particle phase may affect polymer structure, are:

- Molecular weight reduction during process [76, 77];
- Molecular weight and crosslink modification due to interference with the curing process [76];

- Adsorption of polar, low molecular weight species such as surfactants, plasticisers, stabilisers and antioxidants and oxidations products;
- Formation of an immobilised shell of polymer around the particle. Commonly this shell is rich in a certain molecular weight fraction, which is then depleted in the matrix;
- Modification of crystallinity in semi-crystalline polymers [78-80];
- Effects on polymer conformation due to particle surfaces and inter-particle [76, 81].

Lan et al. [82], showed that hybrid organic-inorganic composites typically exhibit mechanical properties superior to those of their separate components. Therefore, there is a synergy between the properties of each material.

In the early studies of using particles as reinforcement, some authors concluded that in general the addition of fillers causes a continuous and drastic reduction in fracture energy, resulting in a brittle, weak product. Besides, sometimes the incorporation of fillers can be quite unpredictable [83]. Nevertheless, nowadays numerous studies show to the research community the opposite. Thus, to be successful in this area, it is necessary to understand all the parameters involved. The properties of the constituent phases (filler and matrix), filler volume fraction, filler particle size and shape, and filler-matrix interfacial strength significantly influence the overall properties in general and failure properties such as tensile strength and fracture toughness [84].

The toughening effect of particles, whatever their nature and properties, depends on their size, interparticle distance, particle/matrix interaction and volume fraction. These parameters must be controlled and tailored for each particular material. In the next section of this review these parameters and how they influence the toughness of the final composite/adhesive matrix are discussed.

4.1-Toughening mechanisms

The mechanisms associated with increased toughness have been extensively studied and several proposals exist, depending on the material type and particle size, yet a great deal of controversy still exists on the nature of the toughening mechanisms [51]. For example, Boogh et al. [85] state that toughness implies energy absorption and can be achieved through various deformation mechanisms before failure occurs and during crack propagation. On the one hand, toughening can be achieved by reduction of the crosslink density or use of plasticizers which lead to increased plastic deformation. This approach, however, may seriously affect the modulus and thermal properties of the material for only a moderate increase in toughness. However, the most effective toughening mechanisms are induced by addition of a second phase in the form of particles.

The main toughening mechanisms proposed in the literature are schematically presented in Figure 4. For example, Bucknall et al. [4] showed that the crazing of a matrix containing rubber particle phase enhances the toughness. On the other hand, Kinloch [86] concluded that the mechanisms of toughening resulting from rubbery particles or phases are: localized shear yielding or shear banding in the epoxy polymer, which occurs between the rubbery particles; plastic hole or void growth in the epoxy polymer, which is initiated by cavitation or debonding of the rubber particles; and rubber particles bridging the crack surfaces. On a different study, Launey et al. [87] refers that shear yielding and crazing are competing when particles are used as toughеners. Shear yielding resembles plastic flow in metals, where molecules slide with respect to one other when subjected to critical shear stress. Crazing, which occurs in glassy polymers subjected to tensile stress, represents highly localized deformation that leads to cavitation. Compared to shear yielding, crazes are more likely ahead of a crack tip because of the fibrils at the trailing edge of the craze rupture. Hence, cavities in the craze zone coalescence with crack tip, similar to microvoid coalescence in metals. Craze crack growth can either be stable or unstable, depending on the relative toughness of the material.

According to Kunz et al. [88] generally, the tensile failure of ductile particles does not implicate the simultaneous breaking of all molecules crossing the fracture plane.

Usually, the molecular chains rupture successively due to the propagation of a tear, initiating at a defect. Therefore, tearing is expected to initiate in a stretched particle at an existing defect at the particle/matrix interface (See Figure 4).

Fu et al. [89] pointed out that the presence of voids is common observed in a fracture surface. The generation of the voids is due to the particles cavitation and is a key part of the dissipation of energy in particle toughened epoxies. It is due mainly to two aspects: cavitation absorb energy and essentially because it encourages the yielding of the polymeric matrix. This process is favoured by the uniform distribution of the particles throughout the matrix.

To conclude, the toughening mechanisms of polymers have been investigated with various effective approaches. A wide range of particle reinforcements have been employed to enhance the mechanical properties in polymers (i.e. strength and toughness). In the next section, the main parameters that influence the particle performance are discussed.

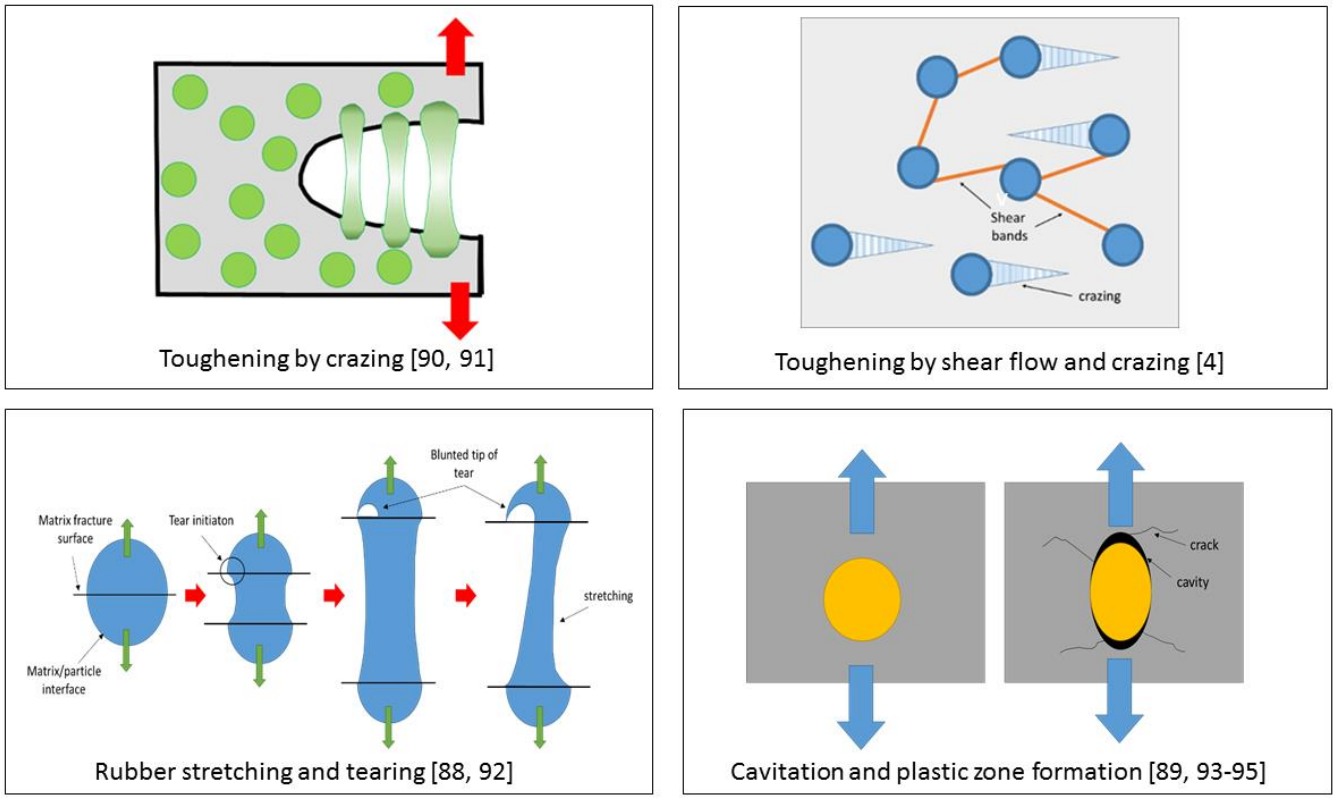


Figure 4 - Toughening mechanisms.

5 – Parameters that influence the particle performance

The properties of the reinforced adhesive do not depend only on the properties of adhesive matrix or reinforcing material. There are other parameters involved in the toughness process (i.e. adhesion between the filler and the matrix), which largely influence the final performance of the composite material. In the following section, the role of the stiffness, volume fraction, size and shape of the particle and the interface particle/matrix, considering always a well-dispersed separate phase in the cured adhesive are discussed.

5.1 - Stiffness of particles

There are several ways to characterize the particles used to improve the toughness of adhesives. There are two major classes: ductile and brittle particles. The next subsection of this review shows the main particles of each class, emphasizing its origin and how they increase the toughness of structural adhesives.

5.1.1– Ductile particles

A very used technique for increasing toughness is to disperse a ductile particle in a harder matrix, helping to dissipate the energy of impact [81]. One of ductile particles with a more widespread use are the rubber particles. Sultan et al. [90, 96] were among the first researchers to show that the fracture toughness of a brittle epoxy could be improved by the incorporation of rubber spheres. Since their initial research, more than a three dozen of different techniques were developed for improving toughness of materials with the inclusion of rubber particles [97]. Although the addition of rubber introduced is responsible for a rapidly increase of the fracture toughness some damaging effects can occur, such as a reduction in the elastic modulus and tensile strength, decreased creep resistance, poor hot/wet performance and a lowering of the glass transition temperature [55, 98, 99]. These particles are typically core-shell particles, with a soft core and a hard shell. Rubber-modified thermoplastics constitute an important class of polymers, characterized by a combination of good fracture

resistance and stiffness. Early studies were made using Polystyrene (PS) as matrix [100]. There are already several years that rubber particles were used to reinforce the epoxy matrix, with a toughness increase, without significantly impairing the other desirable engineering properties. Usually rubber particles are about 1-5 μm in diameter with a volume fraction of about 5-20% [47].

If the matrix is incapable of showing extensive ductility, toughening can be reached by introducing thermoplastic particles, which tend to act by promoting delocalized microcracking as well as crack bridging effects [12, 64]. Rubber particles can induce the formation of microvoids. As a consequence, yielding processes occur due to the reduction of yield stress location. For this scenario, a substantial amount of energy is dissipated within the plastic zone near the crack tip [69]. Bascom and Kinlock [101-104] concluded that the role of ductile particles in toughened epoxies is to relieve the constraint in the matrix by cavitation which, in turn, promotes the formation of shear bands in the matrix. The combination of these two processes exhibit a process zone ahead of the crack tip, which effectively blunts the sharp crack and results in increased toughness. There different mechanisms to explain the toughening effect [88] were proposed. In the first theory, ductile particles act as energy-absorbers [105] or as crack stoppers [106]. However, it is also necessary to observe these mechanisms from the matrix perspective. Observations of crazing [107, 108], induced by the stress-concentrating particles, led to emphasis on the role of the matrix in toughening. Matrix-controlled processes such as crazing, shear yielding [108, 109], and, more recently, combined multiple-crazing and craze-termination [4] are considered the dominant mechanisms of energy absorption in toughening polymers. These mechanisms are generally consistent with the yield behaviour of thermoplastic polymers and rubber-modified crosslinked thermosets (e.g. epoxy, polyester). However, only isolated and largely speculative observations of crazes or bands have been reported [110-112]. Figure 5 show schematically the stages of crack propagation in epoxy resin containing rubber particles. Ductile particles bridge the matrix crack, so as the crack is propagated they are stretches to large strains and fail by tearing. As the crack is wedged further open, first the large, then the smaller particle fail [88].

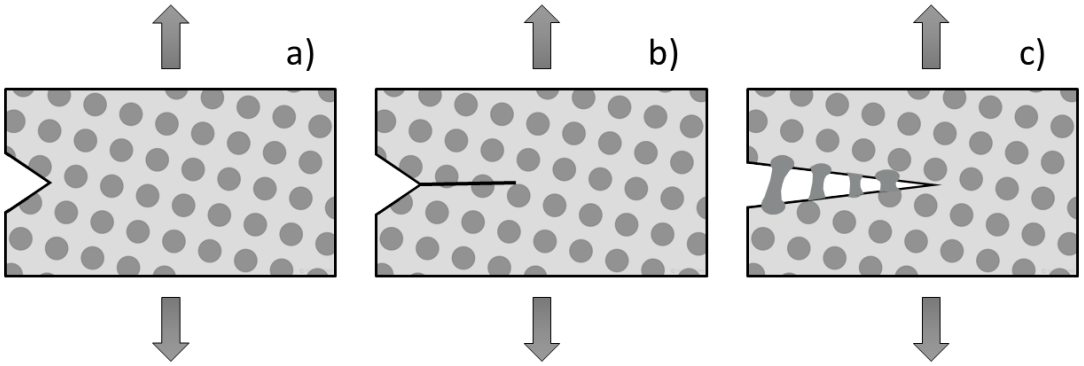


Figure 5 – Schematic diagram showing the stages of crack propagation in epoxy resin containing rubber particles. a) initial crack; b) propagation of crack with ductile particles bridge the matrix crack; c) stretching and tearing of ductile particle.

5.1.2 – Brittle particles

Brittle particles may be organic or inorganic. Inorganic particles are not so effective tougheners (for thermosetting resins) because they do not increase the toughness as dramatically as rubber particles, but they are capable to increase the elastic modulus and hardness much better than rubber particles [19, 113]. For brittle materials, particles with a diameter between 4 and 100 µm are typically used. Calcite, talc, kaolinite, metakaolinite, gibbsite, brucite, muscovite and quartz are some of the types of inorganic reinforcement materials used in plastics [81]. It is the prevailing opinion that these kinds of particles should be avoided, due to their embrittling effects by sharply decreasing the impact energy. In fact, the majority of the studies of modification of semicrystalline polymers with rigid particle fillers show a significant decrease of toughness compared to neat polymers [49]. In these cases, the particles do not work as tenacity promoters, instead, they work as small defects present in the matrix. For inorganic filled epoxies, it is known that the toughening mechanisms are quite different from those in rubber toughened epoxies. Brittle particles also significantly increase the viscosity of the resin, reducing the ease of processing, so it is more common to use nanoparticles [114]. The rigid particles debond from the matrix and create free volume in the blend on a sub-micron size level. The micro-mechanistic model for this toughening effect is shown in Figure 6 [48, 52].

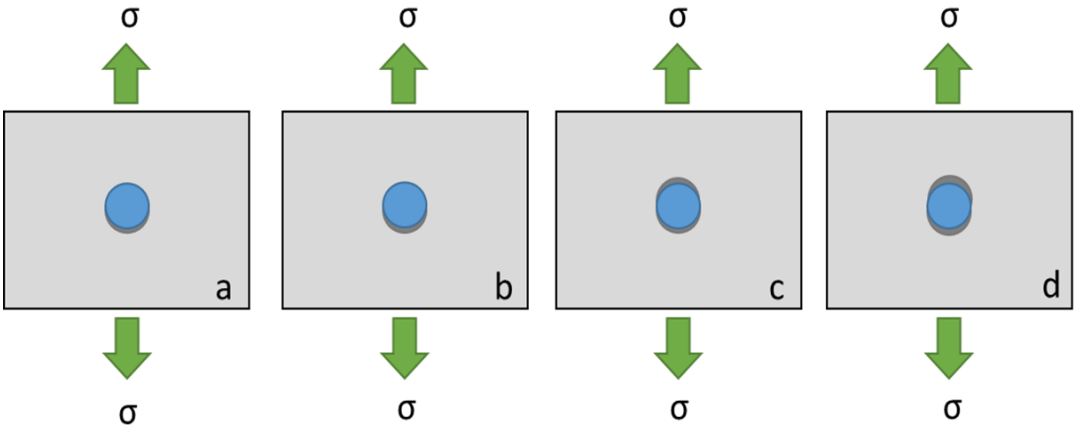


Figure 6 – Failure progression: a) initiation of debonding a tone pole of the particle; b) debonding at poles grows; c) debonding appears at the opposite pole; d) full extent of debonding [52].

The micro-mechanism consists in three stages. The first stage is known by stress concentration. The modifier particles act as stress concentrators, because they have different elastic properties compared to the polymer matrix. The second stage is nominated by debonding. Stress concentration gives rise to build up of triaxial stress around the filler particles and this leads to debonding at the particle–polymer interface. Last stage is known for shear yielding. The voids caused by debonding alter the stress state in the host matrix polymer surrounding the voids. This reduces the sensitivity towards crazing since the volume strain is released. The shear yielding mechanism becomes operative and the material is able to absorb large quantities of energy upon fracture.

There are some studies showing that rigid particles can be used to act as tougheners [49, 115-117]. To do so, they must comply with certain requirements:

- The particles should have a small size (less than 5 µm), otherwise the voids that are created act as initiation sites for the process of fracture. The creation of stable free volume is desired;

- The aspect ratio must be near to one, to avoid high stress concentrations;

- The particles must debond prior to the yield strain of the matrix polymer in order to change the stress state of the matrix material.
- There should be a homogeneous dispersion of the particles in the matrix, avoiding aggregation.

Other criteria that should be taken into account when selecting the particle is the chemical reaction kinetics of cure. The particle could act as a nucleating agent for crystallization or decrease the crystallinity by introducing kinetic hindrance [48, 118].

5.2 – Volume fraction

The volume or the amount of particles dispersed in a structural adhesive matrix is a very important parameter in the resulting properties of the toughening adhesive [37, 61, 103, 119]. The volume of particles is directly related to the nature of the particles and their mechanical properties. Some studies show that moderate increases in the fracture toughness have been observed with low volume fractions of ductile particle [55, 120]. Usually, for ductile particles, G_{Ic} increases only very slowly with volume fraction increase and then reaches a plateau value [103]. For metallic particles, the fracture toughness increases monotonically with the volume fraction particles, for a given particle size [55]. The volume effect on the mechanical properties of an adhesive is very well studied for nanoparticles. Nevertheless, for the particles typically used (i.e. rubber, clay, etc.), when increasing the size of the particles for the micro-scale, the results are not that adequate. Particles of the same material, nano or micro scale present different toughness mechanisms, so it is not possible to extrapolate the effect of the volume of a nano particle size, for the same type of particle in a micro scale.

The mechanics involved in the mechanical phenomena of reinforced adhesives fracture are not only related to particle size, but also to it stiffness and volume of material used. So it is quite difficult to establish a relationship between the volume of material used and the toughness of the adhesive, as it will change according to all other variables. In most cases studied, the toughness increases with increasing volume of particles, reaching a maximum value. After this maximum value of toughness is reached, a

decrease in toughness with increasing the volume of particles occurs (see Figure 7) [121, 122].

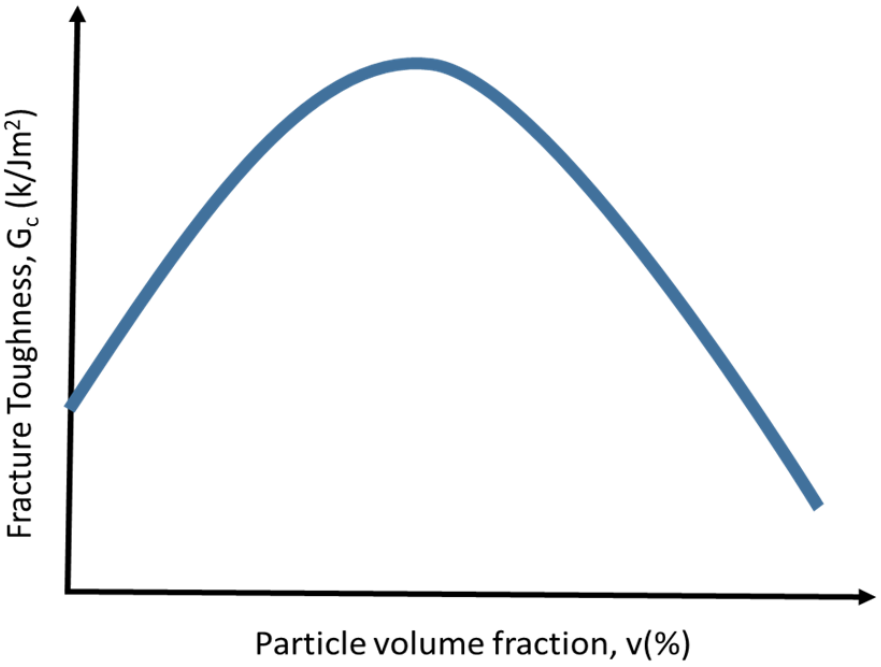


Figure 7 - Effect of particle volume fraction on the fracture toughness, adapted from [121].

5.3 - Size and shape of particles

Particle shape present a great influence on composite stiffness (or rigidity), the viscosity and rheology of a melt or liquid epoxy/particle system, tensile and impact strength, and the surface smoothness of a component, crucial for many of the important properties of a composite. Shape is determined by the genesis of the toughener, by its chemistry, its crystal structure and by the processing it has undergone. Figure 8 shows schematically some particles shapes that can be found in common tougheners.

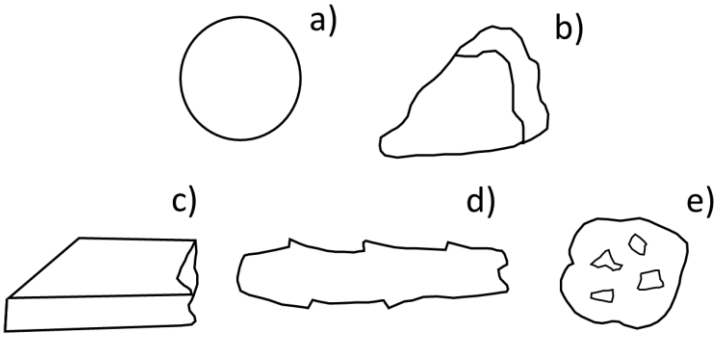


Figure 8- Scheme of some particle types likely to be found in common fillers; a) roughly spherical; b) Irregular; c) plate; d) acicular; e) porous aggregate. Adapted from Rothon et al.[81].

Particle size is a very important parameter and should be evaluated very carefully. The effect of particle size on mechanical performance of thermosetting polymers has been studied by some authors [55, 84, 122]. Some studies [20, 123] showed that, for composites with particles (micro scale), fracture toughness increases with particle size. Nevertheless, this statement is not very consensual. The addition of rigid micro-scale particles to polymers often increases its strength, but decreases the toughness, since the particles may induce stress concentration, which initiates cracks [74]. This is one reason why nano-particles are generally preferred to the detriment of micro-sized particles.

Moreover, particle size is a material parameter that influences not just the fracture toughness but also the operative toughening mechanisms in modified adhesives [119]. Size is a variable that can be controlled, and its importance is felt at all stages of toughening adhesive production and use. Particle size distributions are more useful in reinforcement material studies that single average values. Size can be easily measured using a variety of techniques including sieving, sedimentation, optical scattering and diffraction from particles suspensions. However each technique must be selected according to the particle dimension and shape [81].

In toughening by particle incorporation, particle size and particle properties can be adjusted. The critical stress intensity factor K_{Ic} decreases with an increase in particle size at lower volume fractions, while critical energy releases G_{Ic} drops with increasing

particles size. Figure 9 (left) shows a scheme of the toughness dependency on the particle domain size which display a maximum. This maximum value could be different for other particle sizes for different adhesives. Consequently, a toughening system applicable to various thermosetting matrix materials must include a controllable phase separation process by which particle sizes can be adjusted. Most often, toughening a matrix material is accompanied by a reduction in modulus, according to curve 1 in Figure 9 (right), due to a modification of network structure [85].

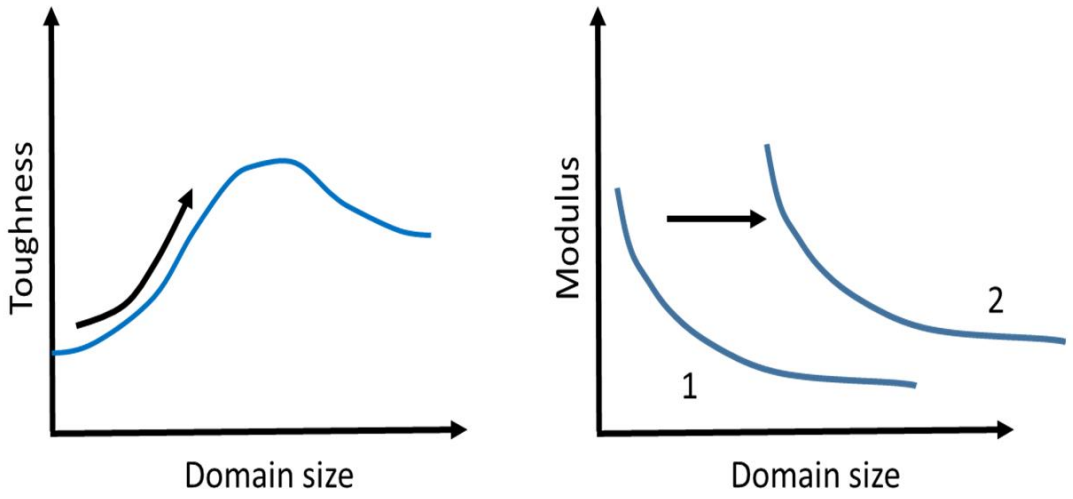


Figure 9- General trends of toughness properties as a function of the domain size of the dispersed phase (left) and the Young's modulus as a function of the toughness properties (right) adapted from [85].

Nakamura et al.[124] studied the effect of particle size on the fracture behavior of an epoxy reinforced with five kinds of angular-shaped silica particles, with sizes ranging from 2–47 µm. Single edge notched beam load in three-point bending (SENB-3PB) were used to measure G_{Ic} and K_{Ic}. They also evaluated the fracture surface of the specimens and verified that with the particle size increase, the toughness also increases. They concluded that the latter is caused by crack deflections around large particles (see Figure 10) [20, 123].

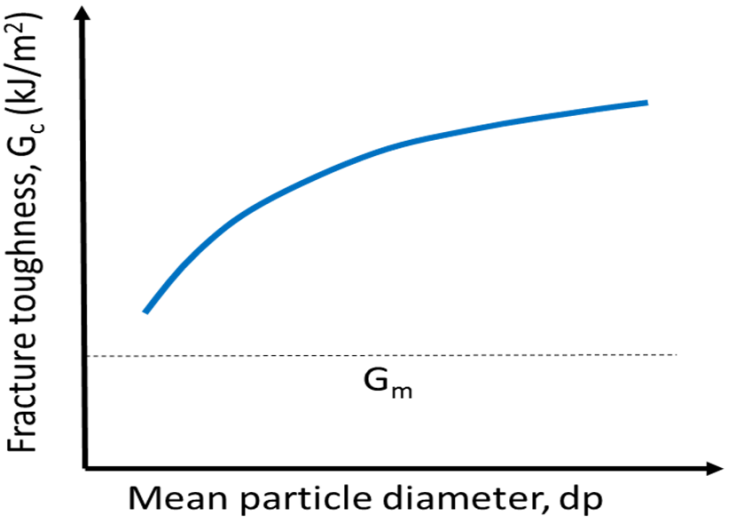


Figure 10 - Particle size effect on the fracture toughness of cured epoxy filled with classified angular-shaped silica particles. The broken line indicates the fracture toughness of unfilled cured epoxy resin. Adapted from [20].

In general, the toughness of bulk adhesives increases with particle size for high particle contents [123, 124]. However, some studies showed that a beneficial effect from bimodal particle size distribution can be achieved (as known as twin population of particle sizes, a special case of wide polydispersity). For example, for bimodal particles the composite presents a craze or mixed (craze/shear) deformation mode. The small particles (bellow one micron) initiate the damage, and the large particles (above one micron) stop and control the crack propagation [42, 43, 125].

Some authors consider that optimized size and shape of the dispersed phase depend on interfacial phenomena and the viscosity of the components [91]. This issue is discussed further for the influence of these parameters on the inclusion of particles as toughening material. In fact, no actual properties can be considered separately. When producing a new adhesive there must be a settlement between all the variables in the production process in order to achieve the desired properties, the easiest to produce and most effective, never forgetting the associated costs.

The importance of size and particle shape is handled at all stages of composite production and application. According to Rothon et al. [81], these factors affect powder

flow, compounding behaviour, composite viscosity, and mechanical, thermal and optical properties. Indeed, most of the current predictive equations for the properties of filled composites use shape and size factors, often using model particles such as glass spheres and flakes. Regrettably such particles are rare in the real world and it is important in applying equations to appreciate the limitations imposed by problems of adequately measuring and describing the morphology of fine particles.

Haubert et al. [46] refers that the term nano or micro composites means to distribute as much as possible amounts of nano or micro particles in a polymer matrix. The basic challenge in order to gain the desired micro- and nanocomposite properties is to disperse the particles as individual particles in the polymer matrix. With decreasing the size of particles, their specific surface area becomes larger, and the probability of particles to agglomerate rises, if no specific surface treatment is applied beforehand. According to Rong et al. [126] and Zhang et al. [127], the particles are very difficult to blend homogeneously with thermoset precursors. Usually a high shear mixing is needed and involves a long and often complex mixing procedure. Moreover, the high blend viscosity does not allow an easy processing.

The properties of the composite are considerably affected by the type of material, but also by the mixing conditions. In ideal conditions, particles must be randomly distributed in the matrix, without agglomeration. Generally, particles of micro-meter sizes are prone to cluster during the composite fabrication. This leads to mechanical properties of micro-composites far below the theoretical values. The particle size ratio of the matrix and reinforcement is the main factor controlling the degree of micro-structural homogeneity. Thus, mixing techniques, such ultra-sounds or centrifuge, are used to solve this problem.

5.4 - Interface particle/matrix

The interface between the particles and the polymer is a very important factor in the toughness process. It is expected that the properties of a composite material, considering a specific surface area, are more strongly influenced in the case of very small particles, since its interface constitute a much higher portion within the bulk material.

Therefore, a good wetting between resin and the particles, promoting a strong bond should be assured. In consequence, particles will act as crack stoppers and not as defects on the matrix. For well-bonded particles, the applied stress can be successfully transferred to the particles from the matrix [20, 128]. Figure 11 shows two examples of a weakly bonded and a strongly bond particle into the matrix [9].

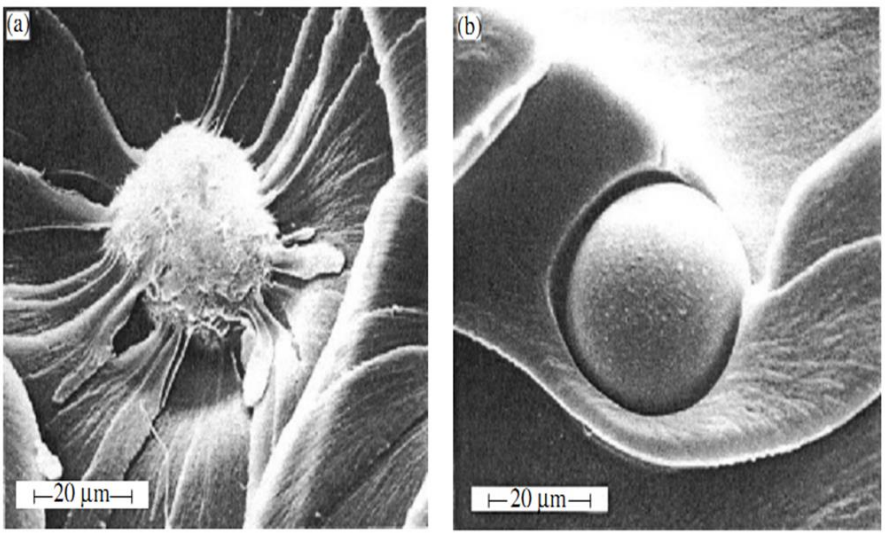


Figure 11 – SEM micrographs of fracture surfaces of PC/glass bead composites (a) excellent interfacial adhesion; (b) poor interfacial adhesion [9].

Kitey et al. [84] performed a study about the role of particle size on glass filled epoxy. They concluded that weekly bonded present lower fracture toughness, compared to strongly bonded particles (see Figure 12). Also, the bonding strength of the particle/matrix interface is an important parameter determining which toughening mechanism is dominant in the filled system (because strengthening the particle/matrix adhesion increases the efficiency of pinning but suppresses crack tip blunting [129]).

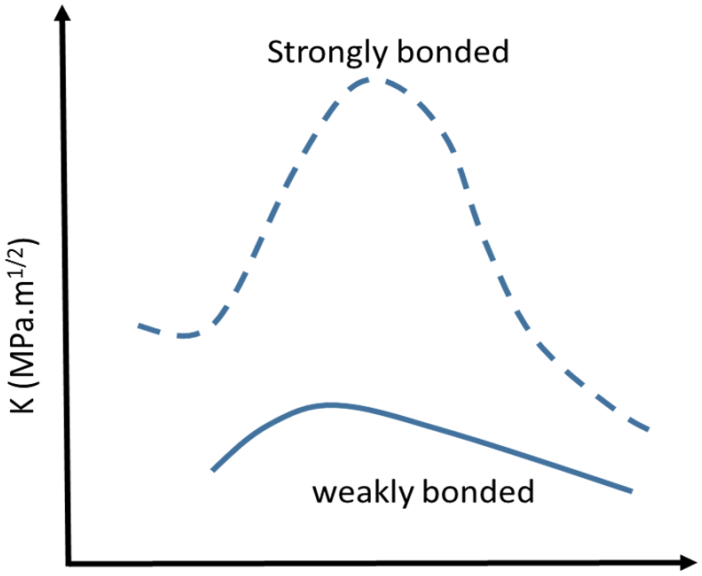


Figure 12 - Particle size effect and the type of bond on steady state fracture toughness. Adapted from [84].

Particle surface chemistries are more important than the bulk ones, as they determine both the rate of wetting and the strength of interaction with polymers. Therefore, to ensure appropriate interfacial interactions their surface properties must be modified accordingly. It is usually recommended that some degree of modification or treatment is applied to all surfaces prior to adhesive bonding. The surface treatments are required to make the surface receptive to the adhesive. According to Herrera-Franco et al. [130], several methods are used to modify the reinforcement's materials (especially naturals) surfaces such as: graft copolymerization of monomers onto the surface, the use of maleic anhydride copolymers, alkyl succinic anhydride, stearic acid, etc. It is also known that the use of coupling agents such as silanes, titanetes, zirconates, triazine compounds improves particle-matrix adhesion. Plasma treatments are also well applied to treat polymeric surfaces [58, 131].

6 – Biological raw-material particles used to increase toughness

Biological raw-material particles are also used as promoters of toughness of brittle adhesives. In this review, a special emphasis is given to cork, once it has been made a greater effort, by the scientific community and industry, to include this material in new applications, especially in Portugal, due to its unique properties.

The increasing of environmental awareness and the implementation of new standards and regulations are forcing industries to seek more environmentally friendly materials for their products. Carbon dioxide neutrality of natural materials is particularly attractive. Burning of substances derived from fossil products releases enormous amounts of CO_2 and another noxious chemical compounds into the atmosphere. This phenomenon is believed to be the root cause of the greenhouse effect and by extension the world's climatic changes [132, 133].

Biological (natural) materials are complex composites whose mechanical properties are often outstanding, considering the resistance of the constituents from which they are assembled [134]. These materials are the result of hundreds of million years of evolution and they inspire materials scientists to biomimic these systems or incorporate them in kwon matrix, in order to design novel materials. Biological materials are anisotropic and generally exhibit one or more of the following chemical elements C, N, Ca, H, O, Si and P. There are several ways of classifying biological materials, this classification can be according to their structure, class of material, elements, scale or shape. Table 2 presents a possible classification of biological materials.

Table 2 – Classifications of biological materials [87, 134].

Structure	Class of material	System	Elements	Scale	Shape
Organic	Polymer	Anysotropic	C, N,Ca, H, O, Si, P	meso	particle
					fibre
Inorganic	Ceramic			micro	whiskers
					foam
				nano	cells

Natural materials have many advantages compared to synthetics, such as: low weight, they are recyclable and biodegradable. They are also renewable and have relatively high strength and stiffness and cause no skin irritations (condition very important for workers who handle raw materials). There are several materials that are inspiring research in the application of natural materials as reinforcements, such as: bone, nacre, wood or some fibers such hemp, coconut, jute, and so on. For example, wood has a high specific stiffness and specific strength that is comparable to steel, due to compounds such lignin, hemicellulose and others [135]. The most notable property of wood it's the highly anisotropic fracture toughness (ten times larger, axial direction, than that of a fibrous composite with the same fraction of fibers and matrix).

Several studies have been performed to evaluate the potential of natural fibres/particles as reinforcements for composites [15, 136-141]. However, most of these studies focus on the stiffness. These materials present good results, but when compared to glass composites, the natural composites do not reach the same level of strength. As discussed above, the use of particles as reinforcement material is not limited only to the increased stiffness. Natural materials offer microstructural design strategies for the development of new materials for structural applications demanding combinations of both strength and toughness [87].

From a fracture-mechanics point of view, it is evident that most of these biological materials derive their fracture resistance through the presence of a series of extrinsic toughening mechanisms acting at several length-scales (synthetic materials). This results in characteristic R-curve behavior with the vital implication that these materials develop most of their toughening during crack growth, not during crack initiation [87].

Due to the morphology of natural materials, in particular those of vegetable origin, they are commonly used in the form of fibres, because these materials have anisotropic properties depending on the direction of growth of the plants. Few are the raw materials of vegetable origin which can be used as reinforcing material in the form of particles. Cork is one of the materials that due to their unique properties can be used in this way. In the next subsection of this review the cork material is presented as a potential reinforcement material for adhesives.

6.1 – Cork as reinforcement material

Several authors characterized cork as a biological material with unique properties, produced by cork oak (Quercus suber L.), constituting the external covering of his stem and branches [142-145]. This species stand out of the oaks mainly for the bulky peel of woven corky (cork), the main interests of cork oak exploration. A study made by World Wide Fund for nature reveals that cork is a truly sustainable product, because it is renewable and biodegradable [146]. Cork harvesting is an environmentally friendly process, during which not a single tree is cut down in the process. The bark renews itself ready for the next harvesting.

Macroscopically, cork is a light, elastic and substantially impermeable to liquid and gas, a thermal and electric insulator and acoustic and vibration insulation absorber, innocuous and also significantly imputrescible (unaffected by microbial activity), with the ability to be compressed without lateral expansion. Microscopically, cork is constituted by layers of cells arranged in honeycomb shape. The cell membranes have a certain degree of sealing, and are filled with a gas similar to air, which occupies about 90 percent by volume. It isn't, however, only the honeycomb shape which gives cork its characteristics, since many of properties are due to the nature of cell membranes. Both macroscopic and microscopic characteristics are quite interesting for engineering applications [147-150].

The scientific knowledge of the properties of cork did not move forward a lot since Ancient Rome, until the intensified production of stoppers. The most popular and the oldest application are the stoppers, but the potential of this material goes far beyond. During stopper production, a large amount of cork is not used because it is unsuitable or is discarded during production. This material is granulated and used in a variety of applications, mainly for production of cork/rubber composite [143]. This composite can be used in automobile industry (joints, level indicators, valves, decoration and other motor components), aeronautical industry (used to coat the front of the aircraft and rockets, used by NASA for more than 50 years) joints for electric and gas equipment, acoustic and vibration insulation (construction, railways), oil spills (cork granules, marine barriers, pads and cleaning floats due to hydrophobicity of the material function as an absorbent of oils and organic solvents without absorbing water. These products are used

in industrial applications but also for the control of oil spills and components for footwear industry [151]. Nowadays, the cork has been applied to the production of new composites, such as sandwich cork composites, cork/thermoplastic agglomerates, lightweight polymer mortar with cork granules, polyurethane elastomeric material with cork filler [152]. Cork based agglomerates are an excellent choice for core material for sandwich components of lightweight structures. The results from experimental tests shown that cork agglomerates performance basically depends on the cork granulate size. Comparing with high performance foams, sandwich components using cork agglomerates present a higher energy absorption capacity and better thermal properties [153]. Also an agglomerate of cork particles with thermoplastic binding agents was developed to use mostly cork powder, the major industrial cork waste, these technologies and products were patented. These new composite are stiff and hard and not resilient and can be used for panels [154]. Other application where cork was a successful filler material was in polyurethane elastomeric material, cork was used for passive isolation. This new cork application can be used as a bearing pad for acoustic and vibration isolation for railway/underground lines [155].

Cork structural properties could be also very useful to reinforce a brittle adhesive, especially to improve the toughness since the closed cells could work to absorb the impact. Cork is a material closed cell with prismatic cells that work together and is a material elastically orthotropic axisymmetric relative to the direction of the tree. However, the properties of an adhesive/cork composite are not only dependent on the material properties, but also on the interfacial adhesion properties between the cork and the resin, size and amount of cork particles and mixing conditions, as already stated in the previous sections [156].

Barbosa et al. [16, 131, 157, 158] performed a research aiming the inclusion of cork particles as toughness promoter in brittle epoxy adhesives. The authors concluded that the use of cork slightly differs from the particles normally used as reinforcements. Firstly, the size is much higher than for example rubber particles, usually is used nano or a few microns particle size. When including cork in epoxy matrix, the dimensions must be above 30 microns (see Figure 13). Below this value, the cork has no effect on increasing the toughness, due to cork particle cell structure.

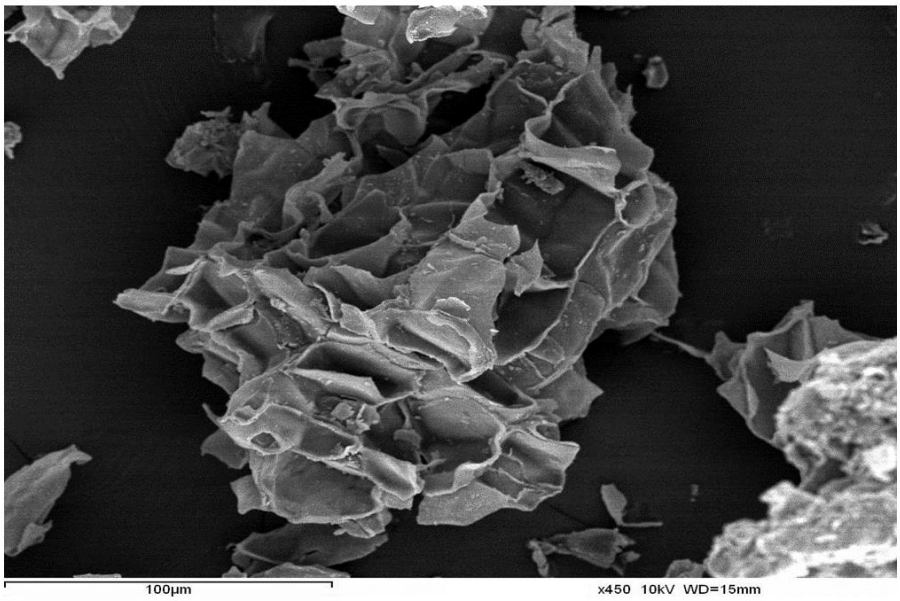


Figure 13 - Cork particle.

The amount of particles is also a key factor in the inclusion of these particles, as has been showed in the previous sections. Barbosa et al. [16, 131, 157, 158] showed that this is also a key parameter, indicating that the final properties of the composite material vary with particle size. However, this issue still needs further study. The main characteristics of the cork derive from the interaction between cells as a whole (the plate, board or particle board), however it was observed that most of the properties of the cork may also be observed in the particles small dimensions. Nevertheless, these particles should have a considerable number of cells, so that they can work together. For example particles of one or two cells no longer have the same mechanical properties as compared to larger particles. Although there are some precautions to be taken when using cork as a reinforcing material, its use is possible and the results are promising [16, 157-159].

7 – Conclusions

A critical review of the theories and experimental results of the mechanical properties (majority toughness) of materials reinforced with particles is presented. It is shown that the toughening effect of particles, whatever their nature and properties, depends on their size, interparticle distance, particle/matrix interaction and volume fraction. These

parameters must be controlled and tailored for each material. The application of new materials such as bio-based materials as reinforced materials was also presented. Currently there is a growing interest from the scientific community and industry, in the use of new particles to increase the toughness of brittle adhesives due to the several advantages that they offer. Depending on the material selected, the use of micro-particles could be less expensive and allow faster product development, compared with other techniques to increase the toughness. Besides increased toughness, other advantages, such as reducing the density of the final adhesive can be achieved. In aerospace and automotive industry this can be a major competitive advantage, since a major concern in this sector is the final weight of the structure. Recently, the scientific community has made a colossal effort to develop and / or use new materials to escape to typical petroleum materials. And the consciousness to use "green" materials is increasing. One such example is the application of light biological materials, which in addition to having very complex and interesting properties, are a new way of reusing materials which have traditionally been regarded as a by-product with little commercial value associated. This opens a new and exciting development opportunities in this area and offer promising potential in the future.

ACKNOWLEDGEMENTS

Financial support by Foundation for Science and Technology (SFRH / BD / 88173

/ 2012) is greatly acknowledged.

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Paper 2

Impact toughness tests: preliminary evaluation of the effect of size, amount and surface treatment

Influence of the size and amount of cork particles on the impact toughness of a structural adhesive

A.Q. Barbosa[1]*, L.F.M. da Silva[2], A. Öchsner[3], J. Abenojar[4], J. C. del Real[5]

[1]IDMEC, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

[2] Department of Mechanical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

[3]Faculty of Mechanical Engineering, Universiti Teknologi Malaysia (UTM), 91310 UTM Skudai, Johor, Malaysia

[4]Materials Performance Group. Materials Science and Engineering Dept.

Universidad Carlos III de Madrid. Av. Universidad, 30. 28911-Leganés, Spain

[5]Department of Mechanical Eng. Universidad Pontificia Comillas, C/

Alberto Aguilera 23, 28015 Madrid, Spain

ABSTRACT

The inclusion of particles (nano or micro) is a method to improve the mechanical properties, such as toughness, of structural adhesives. Structural adhesives are known for their high strength and stiffness but also for their low ductility and toughness. There are many processes described in the literature to increase the toughness, one of the most common being the use of rubber particles. In the present study, natural micro particles of cork were used with the objective to increase the impact resistance of a brittle epoxy adhesive. The idea is for the cork particles to act like crack stoppers and absorb impact leading to higher absorption of energy. The influence of the cork particle size and amount were studied. Particles of cork ranging from 38 to 250 µm were mixed in the epoxy adhesive Araldite 2020® from Huntsman. The amount of cork in the adhesive was varied between 1 and 5% by weight. Surface treatment (low pressure plasma) was applied to the cork powder to assess the effect of the interaction adhesive-cork with several degrees of adhesion. This evaluation was made using impact tests and

it was evident that impact absorption was related to the size and amount of cork particles in the resin, considering a uniform particle distribution.

Keywords: Adhesive; Cork; Mechanical properties; Surface treatment

1. Introduction

Structural adhesives are often the best solution to join two components, in relation to traditional solutions, such as welding, for example. One of the most common structural adhesive, is the epoxy resin. The densely crosslinked molecular structure of structural adhesives is responsible for the good properties of these materials but, unfortunately, it also makes them inherently brittle (low ductility and toughness) with poor resistance to crack propagation [1,2]. The ability of an adhesive to absorb energy without catastrophic failure can be increased through toughening of adhesives with addition of a second phase. This results in enhanced resistance to fracture and impact with minimal change in the gross properties of the matrix resin [3]. The inclusion of particles (nano or micro) is a method to improve the mechanical properties such as toughness of structural adhesives. There are many processes described in the literature to increase the toughness, one of the most common being the use of rubber particles [4]. However, natural materials are gaining attention as reinforcements of polymeric matrices due their thermal properties, low density, low cost, and sustainability of the raw material [5]. Cork is a biological material with unique properties, found in the cork oak, constituting the external covering of its stem and branches. Quercus suber L. is the botanical name for a slow growing, evergreen oak that flourishes only in specific regions of the Western Mediterranean (Portugal, Spain, Southern France, part of Italy and North Africa) [4–6]. Portugal is the world's leading market of this raw material, producing three-quarters of the total production. Cork may be described as a homogeneous tissue of thin-walled cells, regularly arranged without intercellular space. Cork reveals an alveolar structure, similar to a honeycomb, without empty spaces between contiguous cells, which are, therefore, closed units. The dimension of the cork cells differs according to the cork type, even in the same board. Moreover, there are alterations in the dimensions from the spring cells to the autumn cells, ranging from 10 to 40 µm [7–9].

These structural properties could be very useful to reinforce a brittle resin, especially to improve the toughness, as the closed cells could work to absorb the impact. However, the properties of a resin/cork composite are not only dependent on the materials, properties, but also on the interfacial adhesion properties between the cork and the resin, the size and amount of cork particles, and the mixing conditions [5]. Cork is hydrophobic due the suberin (main component of cork composition) and this fact can deteriorate the adhesion between cork particles and the epoxy resin. The hydrophobic properties can be altered using surface modification. It is usually recommended that some degree of modification or treatment should be applied to all surfaces prior to adhesive bonding [3]. Cork is a heterogeneous natural material that exhibits variability according to the cork board's origin (geographic, location of the board on the cork oak tree, etc.) and the direction of cork growth. Therefore, adhesion between cork and epoxy resin relies on physical (mechanical interlocking) and chemical bonds. Because cork is inherently porous, the epoxy resin will penetrate into the cork particle cells for mechanical interlocking, but the most durable bonds occur when the adhesive diffuses into cell walls to build chemical bonds with the cell's chemical components [3]. There are several surface treatments to improve the cork-matrix adhesion with a positive effect on the mechanical properties of the composite [5]. Plasma treatment is one of the most versatile techniques in surface modification. Atmospheric pressure plasma is useful to activate the surface and improve adhesion. This activation consists in grafting chemical functionalities on the surface in order to increase its surface energy. The plasma composition influences the treated material's properties. Low pressure plasma is very useful when it is necessary to treat complex sample geometry such as cork powder. This technique also applies no thermal or mechanical strain on the substrates [10]. The cork particles may create obstacles to the propagation of the cracks, thus increasing the toughness of the adhesive. This fact occurs because cork presents a remarkable combination of properties. Cork is a cellular material with prismatic close cells that work together and is an elastically orthotropic material with axial symmetry in relation to the direction of the tree. But cork cells present this excellent behaviour only when a group of a few cells is present. A unique cell of cork does not present this behaviour. Therefore, only a particle with a considerable number of cells may exhibit a damping effect and increase the impact absorption of the resin [11,12].

Besides being apparently technically possible, this technique would also permit a new application for cork powder, which is not well exploited by the cork industry that has an important impact on the Portuguese economy. Cork powder is generally burnt leading to unnecessary energy consumption and frequent accidents. The use of this material would give a new application perspective to the cork industry with potential benefits. Therefore, different amounts of cork and different particles sizes were added to a brittle epoxy to analyse the influence of these particles on the impact behaviour of cork/resin composite.

2. Experimental

2.1. Materials

Cork powders with different sizes (38–53 μm and 125–250 μm) were used. The cork powder and cork boards used for preliminary surface treatments studies were supplied by Amorim Cork Composites (Mozelos, Portugal), without any treatment. The selected adhesive was Araldite 2020®, from Huntsman Advanced Materials (Pamplona, Spain). This is a two-component adhesive (100/30 by weight), low viscosity (150 mPa.s), transparent epoxy adhesive that cures at 100°C, within 15 minutes. The Young's modulus of this adhesive is typically 3100 MPa. This material was selected because it is rather brittle (see Fig. 1), so the improvements on the toughness after inclusion of the cork particles can easily be observed.

2.2. Manufacture of Specimens

A homogeneous mixture of the cork powder in the resin must be assured to avoid the introduction of air bubbles and produce a uniform distribution of particles. The cork was mixed with the resin using a centrifuge mixing machine, SpeedMixer DAC 150TM (Hauschild, Hamm, Germany), during 90 seconds at 1500 rpm. Initially, cork was mixed with the resin and after that the hardener was added to the mixture. This procedure was the same for the different sizes and amounts of the cork. The mixing assures that particles do not agglomerate and are randomly distributed in the resin. Specimens with

and without cork, with different surface treatments and different amount and cork particle size were manufactured, according to Fig. 2.

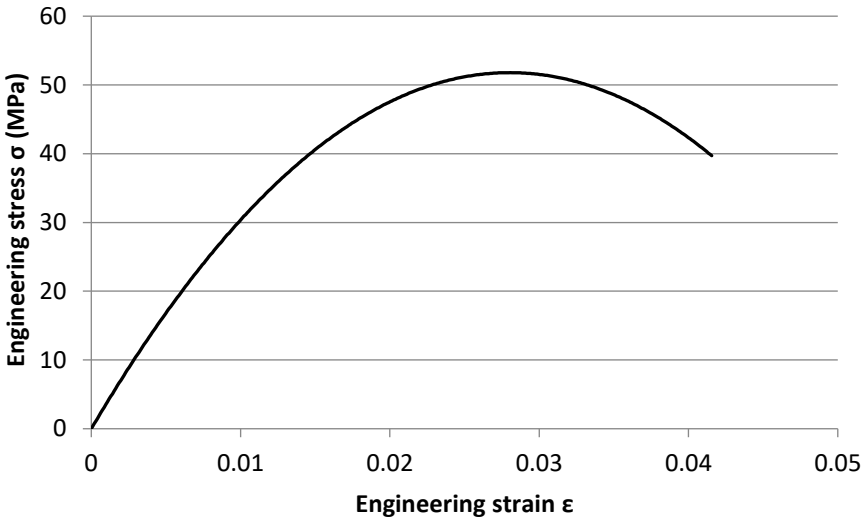


Figure 1 – Bulk tensile stress-strain curve of Araldite 2020®.

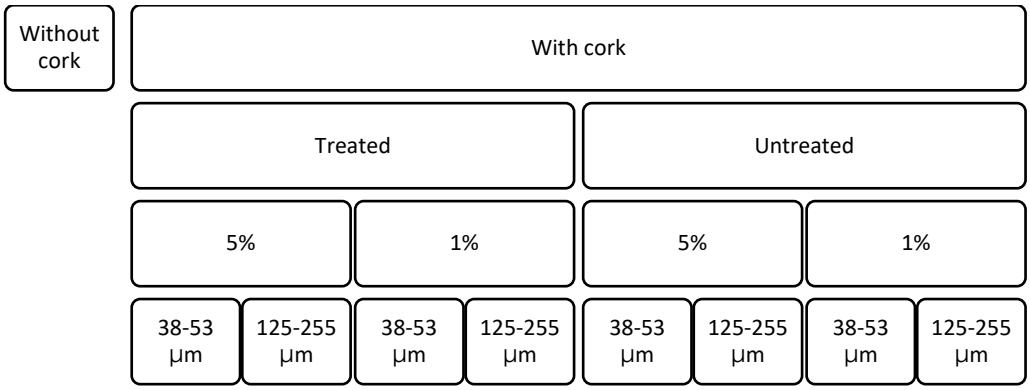


Figure 2 - Schematic diagram of cork specimens with different surface treatments, sizes, and amounts of cork (% by volume).

After mixing the cork particles with the resin and hardener, the mixture was cast in a pre-heated steel mould. Release agent was applied to the mould to ensure easy release of the bulk specimen. A silicone rubber frame was used to apply a hydrostatic pressure to the adhesive, which were hot pressed (2 MPa) for 15 minutes at 100°C (according to the manufacturer's recommended cure schedule), as shown in Fig. 3. Specimens were machined from the plates manufactured with the mould [13]. To assess the dispersion

of the cork particles in the adhesive, thin layers of 5 µm cut by a microtome were analysed in a Leica optic transmission microscope (OTM) (Wetzlar, Germany). The cork particles were coloured with methylene blue for better identification.

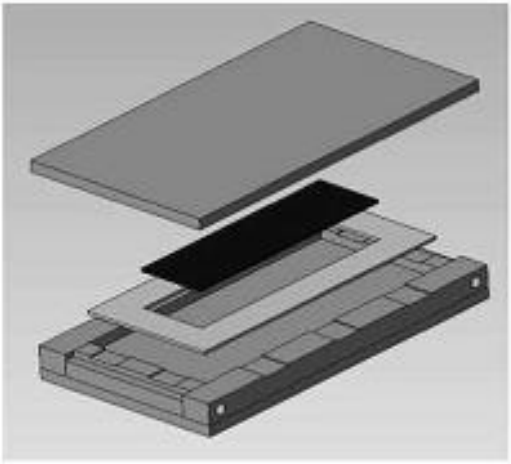


Figure 3 - Mould for bulk specimens. Expanded view with steel plates and silicone rubber frame [13].

2.3. Surface Treatments

Plasma treatment was used to modify the cork particles surface, since, depending on the selected gases, it can increase substantially the surface wettability and decrease the contact angle. There are several proposed models which admit that plasma treatments reticule the subtract surface, developing a more active surface and an improved wettability, due to surface oxidation, introducing reactive groups that increase the surface reactivity. Several preliminary tests were carried out with atmospheric plasma and low pressure plasma treatment on cork boards. Because of the light weight of cork particles, low pressure plasma should be used to avoid the particles dispersion [10,14].

The atmospheric plasma equipment used was a Plasma Treat GmbH (Steinhagen, Germany), which works in a frequency of 17 kHz and a high tension discharge of 20 kV and a rotatory torch (1900 rmp). This system has a platform that allows controlling the treatment velocity automatically. These treatments were made at a distance of 8 mm from the surface and a velocity of 5 $m.min^{-1}$, on cork boards of 100 x 200 x 13 mm.

Low pressure plasma treatment was set on a chamber Plasma Cleaner of Harrick Plasma (Ithaca, NY, USA), using air as gas to produce plasma, at 300 militorr of pressure. An electric power of 18 W and 40 seconds of permanency on the chamber were used.

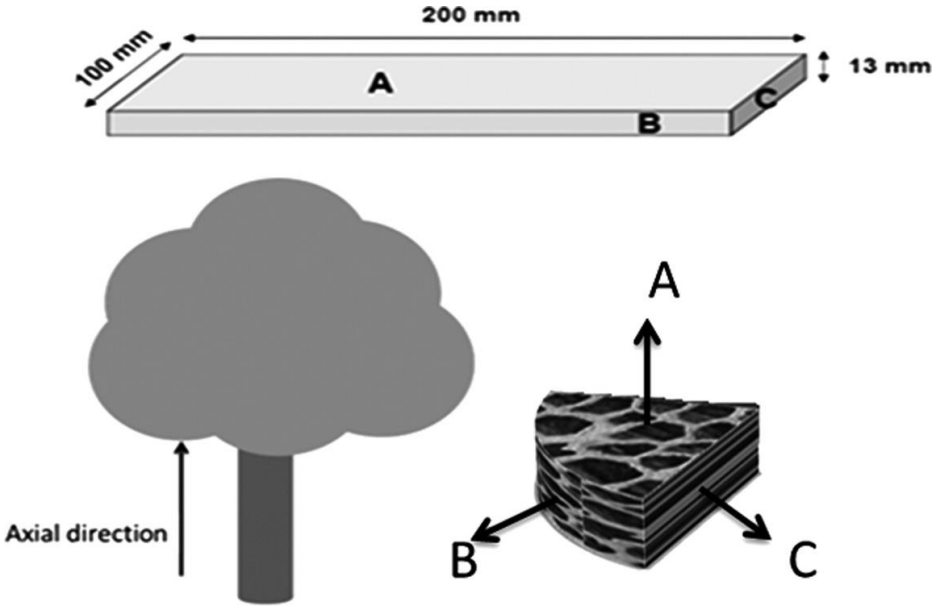


Figure 4 - Top—Schematic representation of the cork sections in the cork board. Bottom—Spatial description diagram of cork structure showing the axis system and sections nomenclature, with schematic representation of cellular disposition in cork.

2.4 – Contact angle and surface energy determination

Contact angle measurements can be related to surface tensions or energies using Young´s equation [15]:

$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}} cos\theta \quad (1)$$

Where θ is the measured contact angle (°) and γ is the surface energy (dyn.cm^{-1}) and the subscripts SV stands solid-vapour, SL for solid-liquid and LV for liquid-vapour. Depending on the used model, an expression for γ_{SL} can be combined with Young´s equation and results in a relation between the contact angle and the liquid's surface tension from which the solid´s surface energy can be calculated with the Owens-Wendt-Rabel-Kaelble (OWRK) method. OWRK method discerns between polar and a dispersive fraction of the surface energy and uses a geometric mean of these in the expression for γ_{SL} [15]. The

wettability of materials was evaluated using a goniometer OCA 15 (DataPhysics, Neurtek Instruments, Eibar-Spain). To evaluate the contact angle, samples were placed in saturated chamber (25°C) with vapour of the liquid used in the measures. The used liquids were distilled water glycerol (polar liquid), diiodomethane (non-polar liquid). These three liquid allow to obtain the cork surface energy.

2.5. Density

The density of treated and untreated cork particles was measured, using a helium pycnometer micromeritics AccuPyc 1330 (DataPhysics, Neurtek Instruments, Eibar, Spain). The density of the impact test specimens was measured based on the Archimedes principle.

2.6. Toughness Impact Tests

To evaluate the mechanical properties of the composite resin/cork, several specimens were made varing the amount of cork, size of particles, and surface treatment. Impact Charpy specimens according ASTM E23-02a were manufactured. Figure 5 shows the dimensions of machined specimens. The toughness impact tests were carried out in a Rosand V1.01 machine (Rosand Precision, Ltd., Stourbridge, UK), an instrumented failling weight impact machine. This test was made with a mass of 4 kg (5 J of available energy), at room temperature and with an initial velocity of 1.57m/s. Three specimens were tested for each condition.

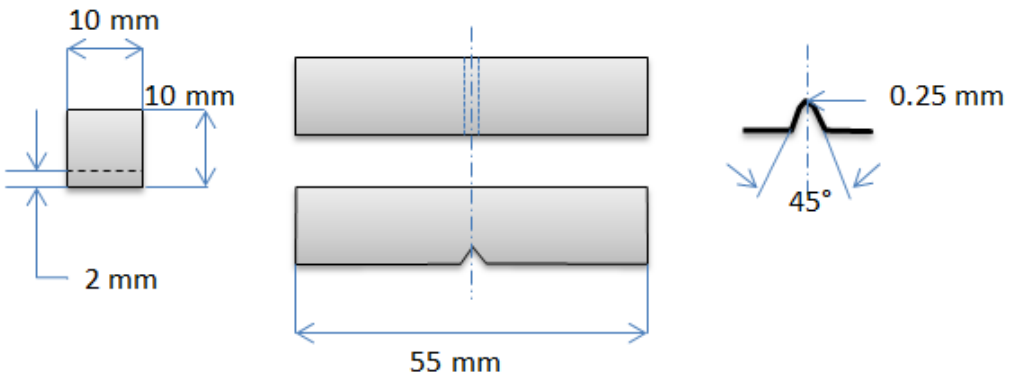


Figure 5- Dimensions of type A Charpy Impact test specimens.

2.7. SEM Analysis

Scanning electron microscope (SEM) analyses were obtained in a JEOL JSM 6301F Oxford INCA Energy 350 Gatan Alto 2500 microscope (Tokyo, Japan). This equipment was used to analyse the cork particles and to analyse the fracture surface of the composite after the impact tests.

3. RESULTS AND DISCUSSION

3.1. Surface Properties of Cork Board

Figure 6 and Table 1 show that with atmospheric plasma treatment, the contact angle between cork surface and the water drop decreases. With surface treatment, cork changes its hydrophobic behaviour to hydrophilic. Table 1 shows that the contact angle does not change with the section orientation analysed. This indicates that the adhesion of the cork particles will be uniform throughout the surface of the cork particles. Figure 7 shows the cell structure of a treated and untreated cork board. In the images of treated cork (atmospheric plasma), an erosion of cork cell walls is evident. Roughness is difficult to evaluate since there are several imperfections on the cork surface. Contact angle results (Table 1) are consistent with the results obtained for surface energy, see Fig. 8. It can be observed that the surface energy of cork increases with surface treatments (atmospheric plasma and low pressure treatment). The increase of the dispersion component is practically the same for both surface treatments; however, the low

pressure plasma treatment shows a slight increase of the polar component compared with the atmospheric plasma treatment. This increase in surface energy values may be responsible for an increase of the adhesion between the cork particles and the epoxy resin.

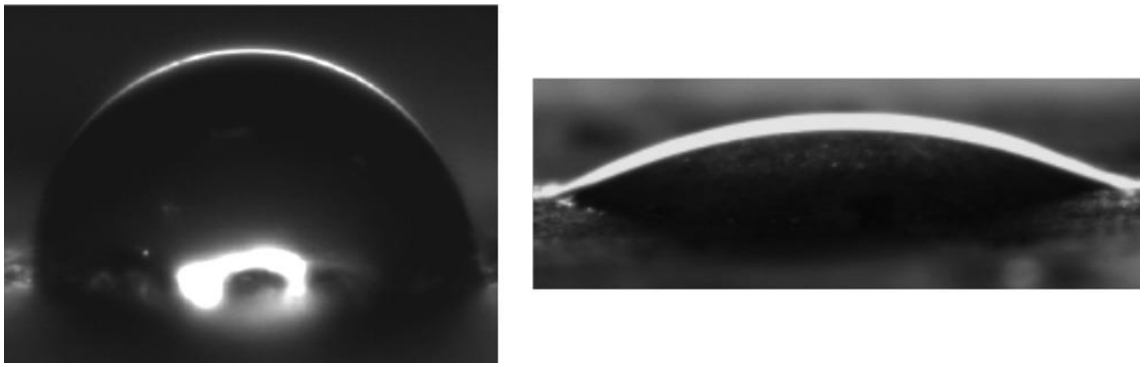


Figure 6 - Shape of the water drop on cork surface, (left) without treatment and (right) with atmospheric plasma treatment.

Table 2 - Contact angle between water drop and cork surface.

Section	Treated specimen	Untreated Specimen
Radial	30 ± 4	101 ± 11
Tangential	33 ± 7	99 ± 18
Axial	37 ± 2	103 ± 7

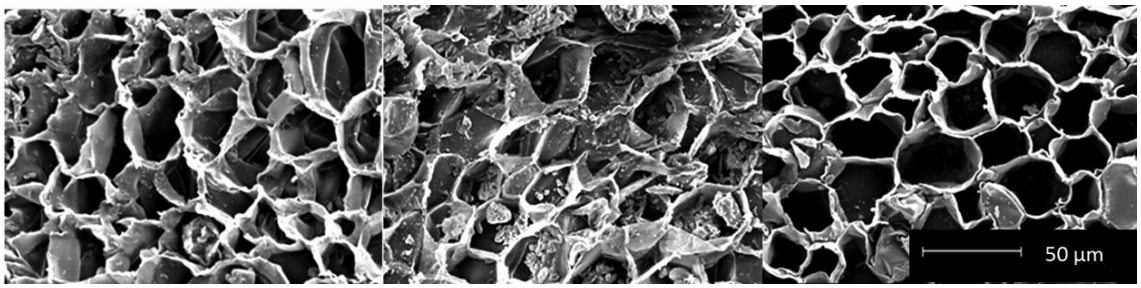


Figure 7 - Cell structure of the cork board. Left—untreated cork board; Center—treated with atmospheric plasma; Right—treated with low pressure plasma [14].

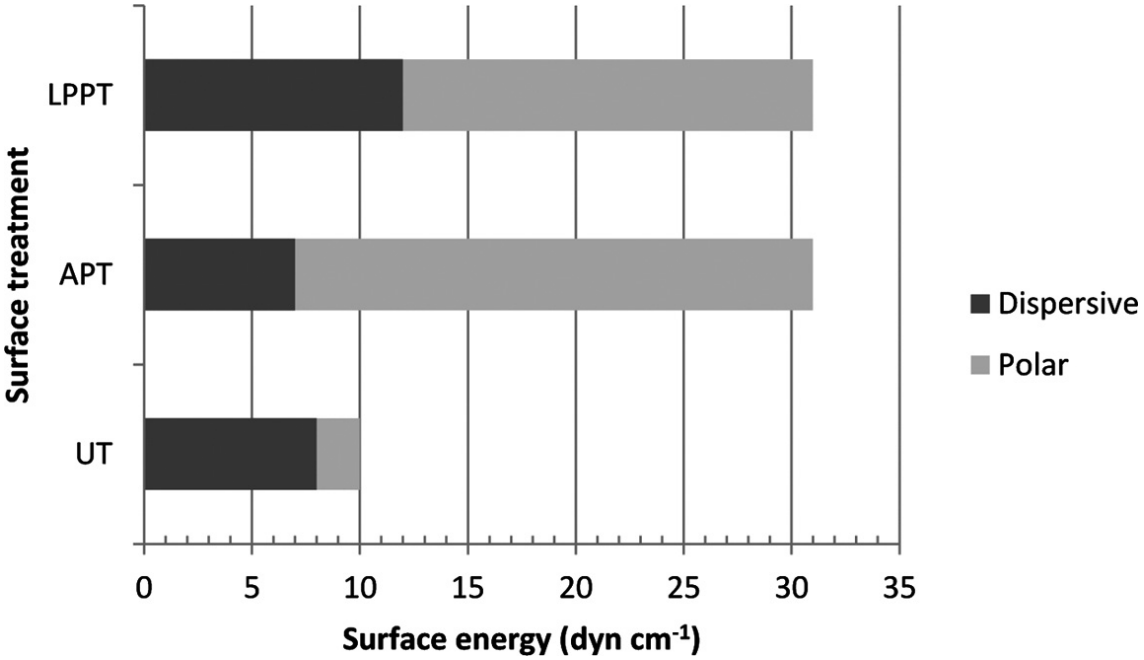
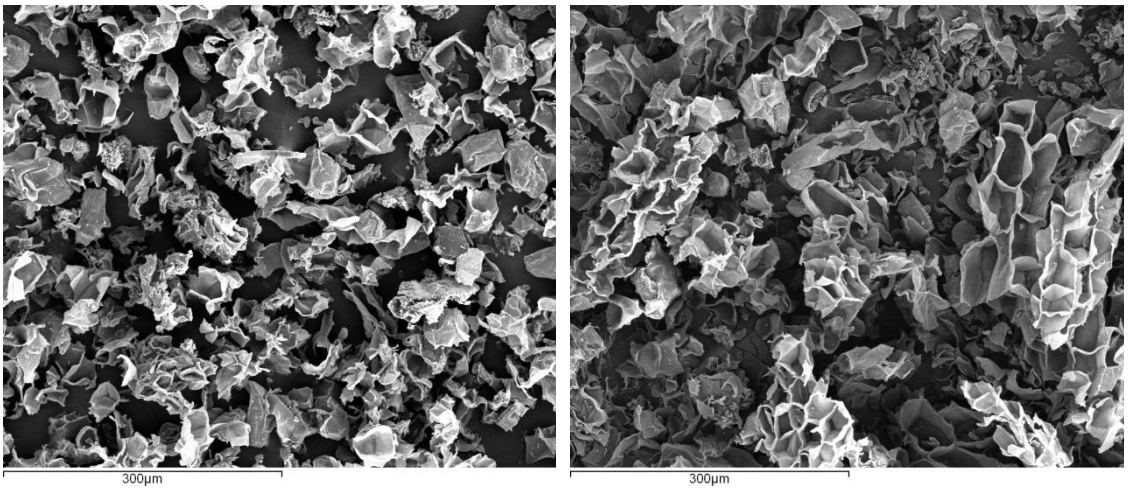


Figure 8 - Variation of surface energy components with surface treatments on cork board. UT—untreated; APT—atmospheric plasma treatment; LPPT—low pressure plasma treatment.

3.2. SEM Cork Particles Characterization

The cork particles, size and shape were analysed in the SEM. Figure 9 shows that particles without surface treatment with different sizes have different cell structures. Particles with 38–53 µm have a damaged honeycomb cell structure, with several cells presenting an open structure and some only a single cell. On the other hand, particles with 125–250 µm size have a honeycomb structure composed of several cells, some open (edges of particles), but a few cells closed (particle core).



a) b)

Figure 9 - Microstructure of cork powder without surface treatment; a) particles with 38-53 µm size, b) particles with 125-250 µm size.

3.3. Cork Powder Density

Cork powder density changes with atmospheric plasma treatment. Figure 10 shows the density of cork particles with different sizes and treatments. The density decreases with plasma treatment. This effect may be due to the plasma eroding parts of the cork surface, leading to a weight loss.

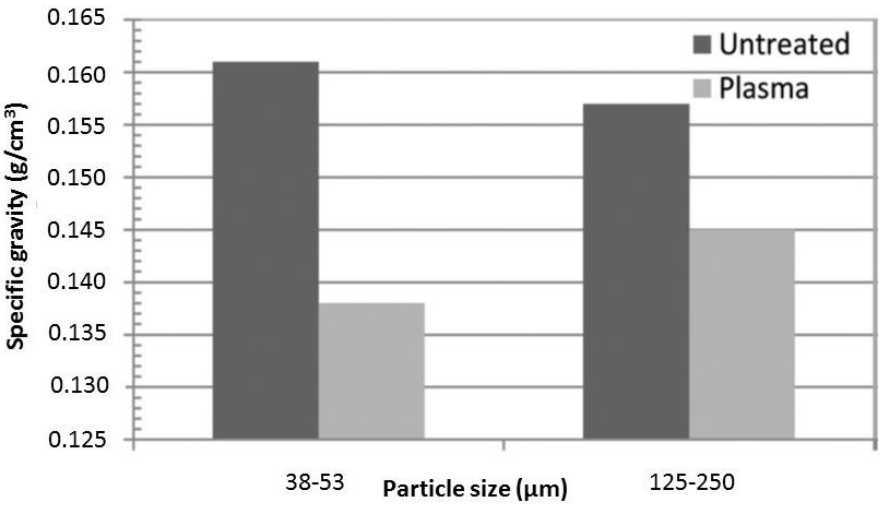


Figure 10 - Density of cork particles, with different sizes, untreated and with atmospheric plasma treatment.

3.4. Toughness Impact Properties

Figure 11 shows a force-time curve. Two important points are indicated in Fig. 11, the maximum force (peak load) and the specimen rupture. Figure 12 shows the variation of the energy absorbed in the impact at the peak load and at rupture. Figure 13 shows the displacement of the specimens during the test, for the two points. It is evident that specimens without cork have a different behaviour compared with specimens with cork. Specimens with 1% of untreated particles with 125–250 µm size have a distinctive behaviour. These specimens show a better behaviour compared with the other composite specimens. They absorb more energy at rupture and give a higher displacement at failure.

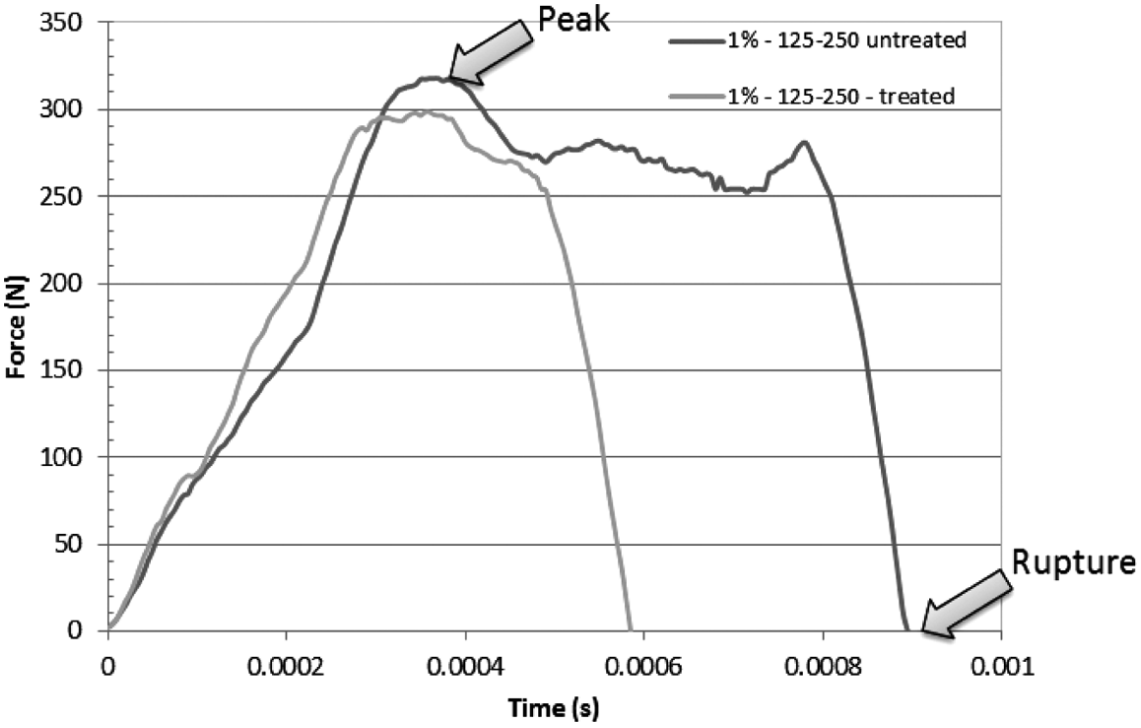


Figure 11 - Force-time curves obtained in impact tests.

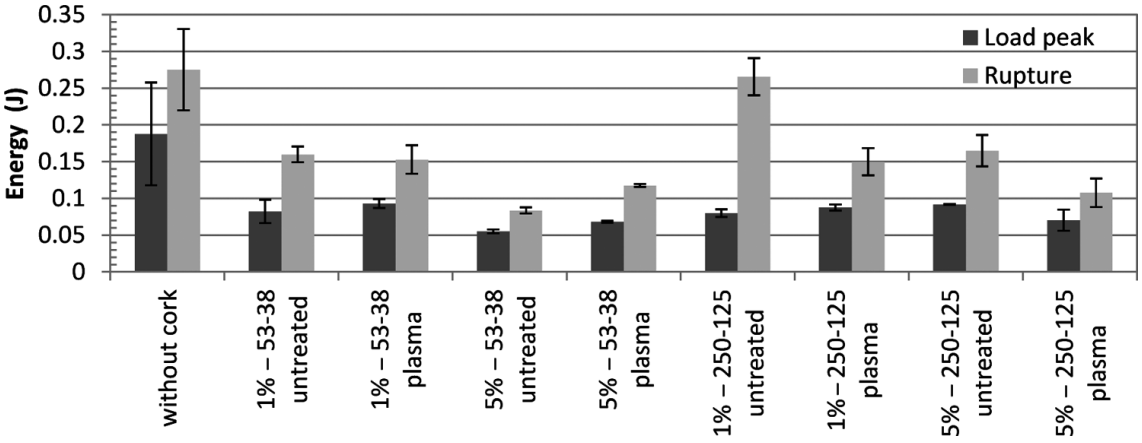


Figure 12 - Energy absorbed in the toughness impact tests, at the peak load and at rupture.

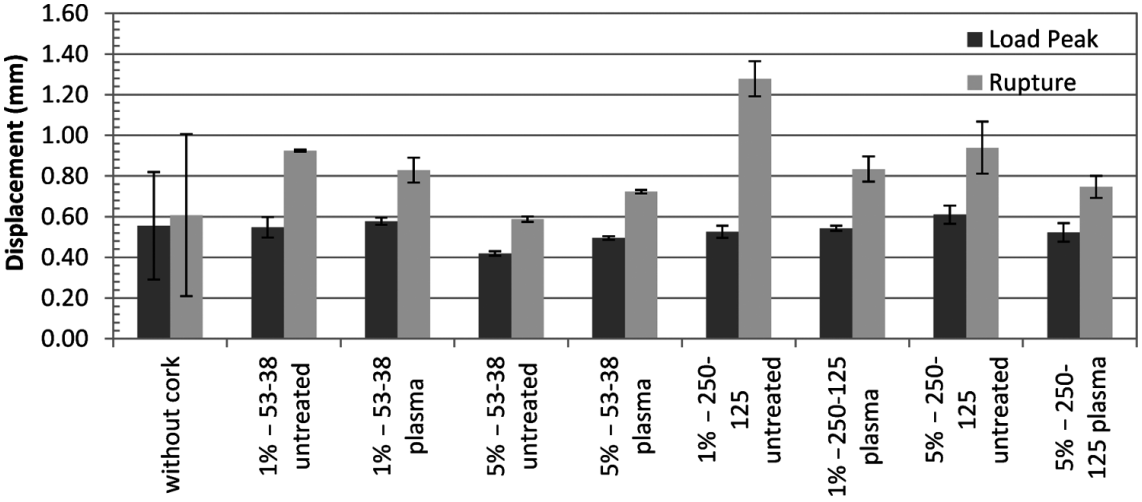


Figure 13 - Displacement of the specimens in the toughness impact tests, at the peak load and at rupture.

Cork has a good impact behaviour due to its cell structure disposition, giving a damping effect. The cells compress, absorbing the impact. But if in the composites the particles do not have an intact cell structure, this effect disappears. Figure 14 shows schematically the damping effect of cork cells with and without resin penetration into the cell interior. When the cells are filled with resin, they cannot absorb energy because the resin does not allow the cell deformation (Fig. 14a). On the other hand, when cork cells have air inside and wall cells are well preserved, when the cell suffers an impact force it can deform, and absorb the impact. Therefore, specimens with small particles show less improvement than particles with the 125–250 µm size, because most of the time these particles have open cells (see Fig. 9). When in contact with resin, cork particles are surrounded by resin but resin might not penetrate into the cell. Figure 15 shows images

obtained with optical transmission microscope. (OTM) and it can be seen that the cell core remains without resin; this was observed for particles with 125–250 µm size. The behaviour of the cork/resin composite is also influenced by the number of cells in the particle.

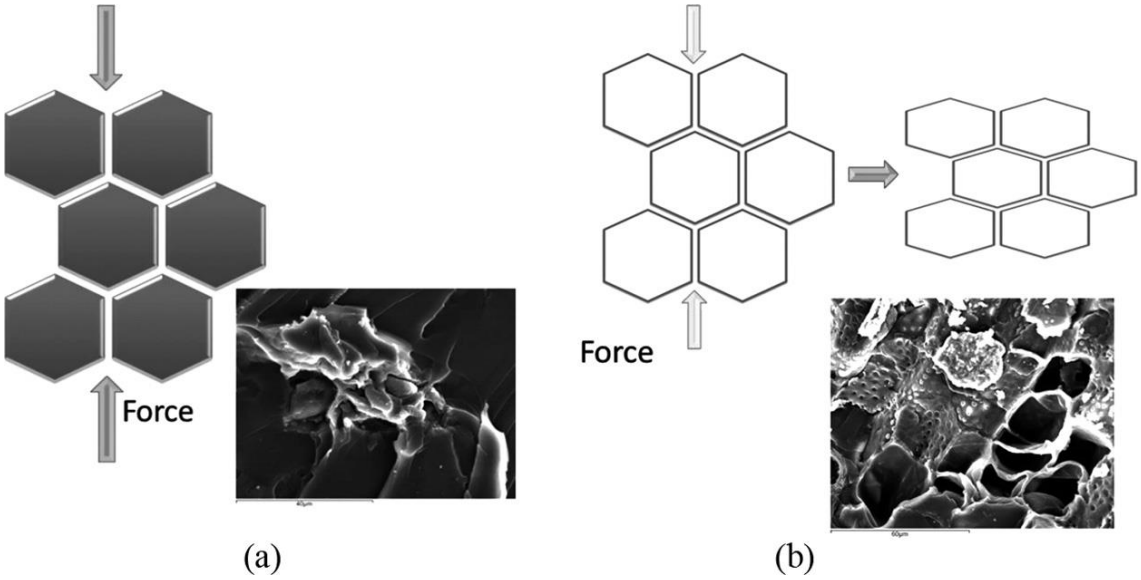


Figure 14 - Schematic representation of the effect of damping of cork cells. (a) cork cell filled with resin; (b) cork cell without resin penetration.

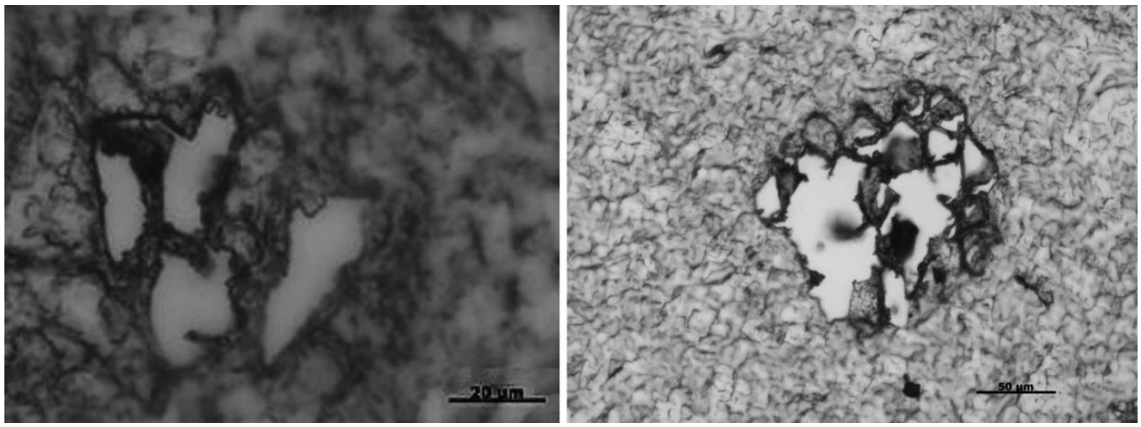


Figure 15 - Resin with cork particles obtained with OTM. Left—closed cell structure, untreated cork particle; Right—destroyed cell structure, plasma treated particle.

Figures 14 and 15 show that the plasma treatment gives worse results than untreated cork particles. This treatment improves the contact angle and the wettability, improving the adhesion between cork and resin. However, this treatment at the same time destroys part of the honeycomb structure of the cork cells. In addition, the damage of

the cork particles can facilitate the resin penetration which could decrease the damping effect of the cork, decreasing the absorption of energy. The differences in the density of the specimens (with or without cork particles) may be related to the adhesive's penetration into the cork particle. If the resin penetrates inside the cork cells, the specimen's density increases, compared with the specimen without cork. However, Fig. 16 shows that the density variation is not substantial, considering the associated error. Therefore, this interpretation may be regarded with caution. Specimens with 1% of cork untreated particles (125–250 µm) presented the best combination of cork amount and particle size in terms of impact toughness behaviour. These particles have an undamaged cell structure that works together with the resin to increase the energy absorption of the composite.

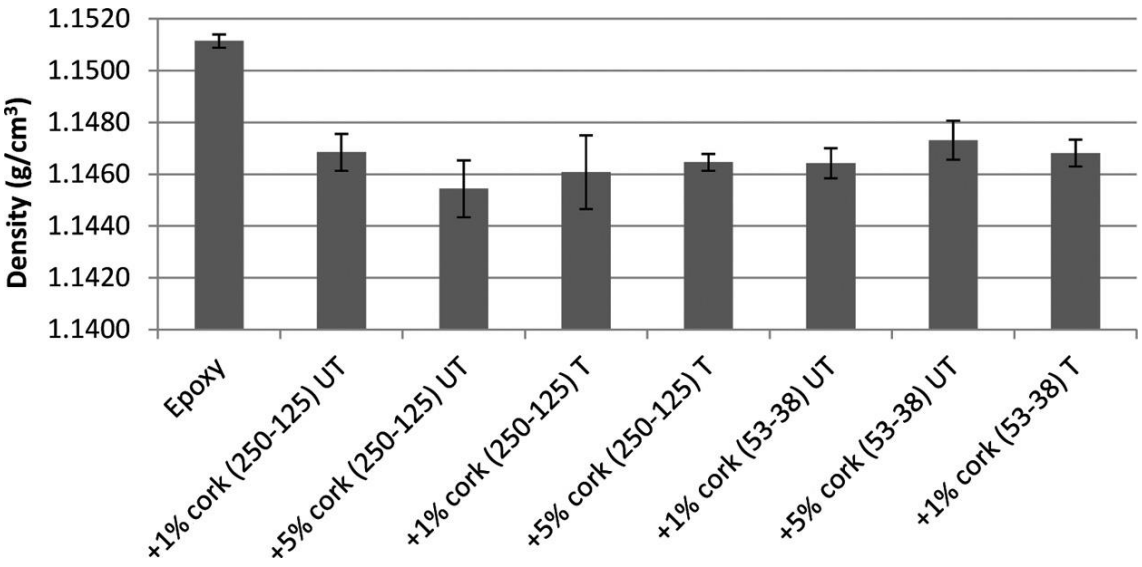


Figure 16 - Density of composite specimens with different surface treatments, amount, and size of cork particles. T—treated; UT—untreated.

3.5. SEM Surface Fracture Analysis

The fracture surface of the impact test specimens was analysed by SEM. Figure 17 shows the fracture surface of a specimen without cork and a detail of fracture propagation. Figures 18 and 19 show the fracture surface of specimens with 1% of cork particles of size 38–53 µm (untreated and treated, respectively). These surfaces show a more brittle behaviour compared with that of the resin without cork because the surface is

smoother. Figures 18 and 19 are quite similar and show (detail of fracture surface) that the cork particle might be a location for crack initiation.

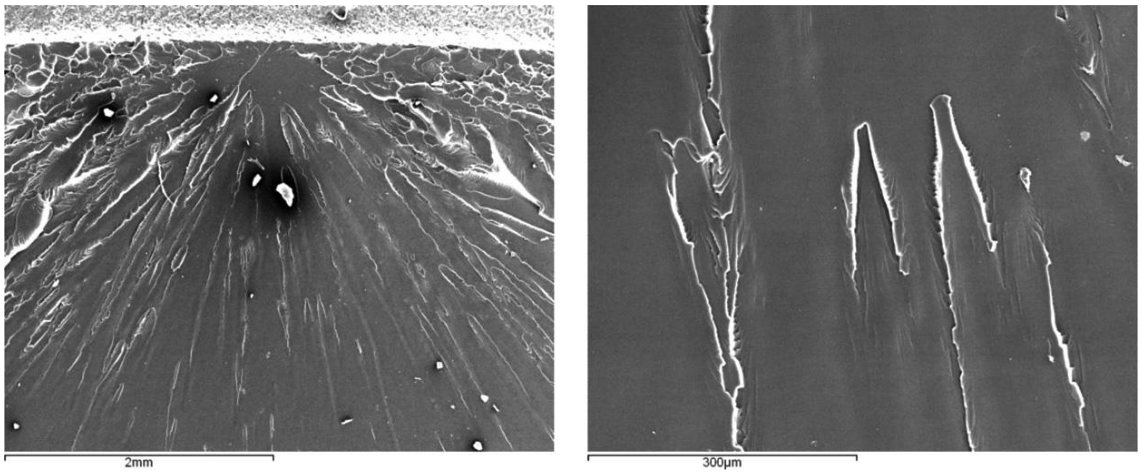


Figure 17- Fracture surface of a specimen without cork. Left—overview of fracture surface; Right—detail of fracture surface.

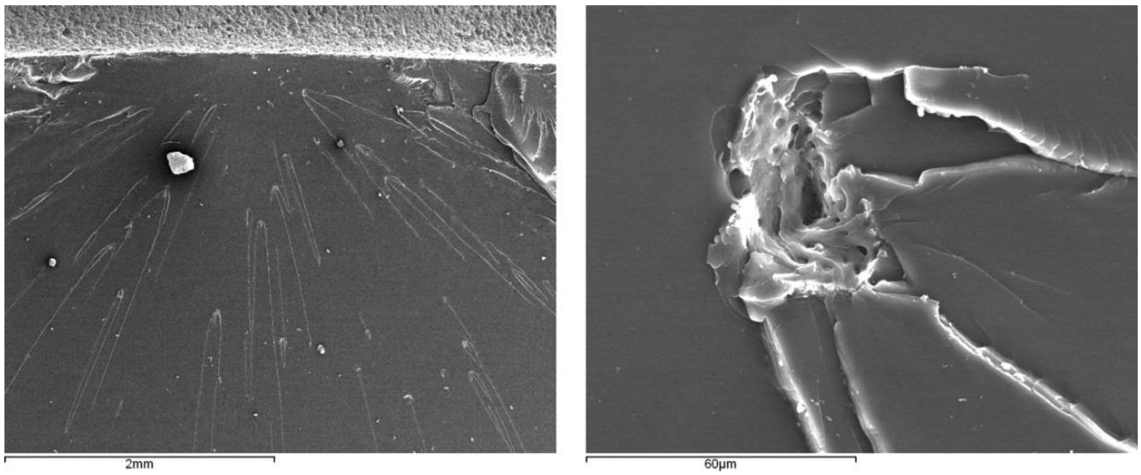


Figure 18 - Fracture surface of a specimen with 1% of untreated cork (38–53 µm). Left—overview of fracture surface; Right—detail of fracture surface.

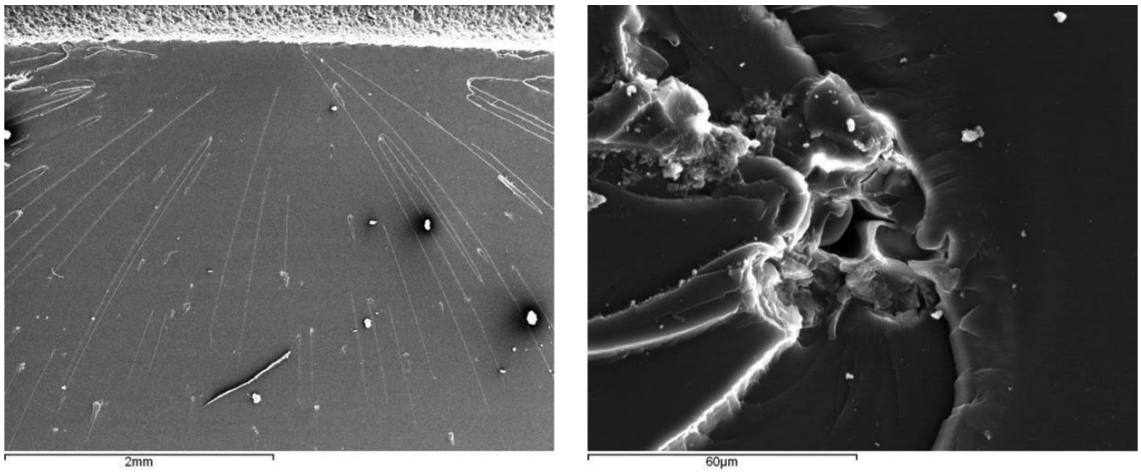


Figure 19 - Fracture surface of a specimen with 1% of treated cork (38–53 µm). Left— overview of fracture surface; Right—detail of fracture surface.

Figures 20 and 21 show the fracture surface of specimens with 5% of cork particles, 38–53 µm size, untreated and treated. There are some differences between these fracture surfaces. Figure 21 shows a more brittle fracture (compared with specimens without cork), and some of the cork particles are filled with resin, preventing these cells from absorbing impact energy.

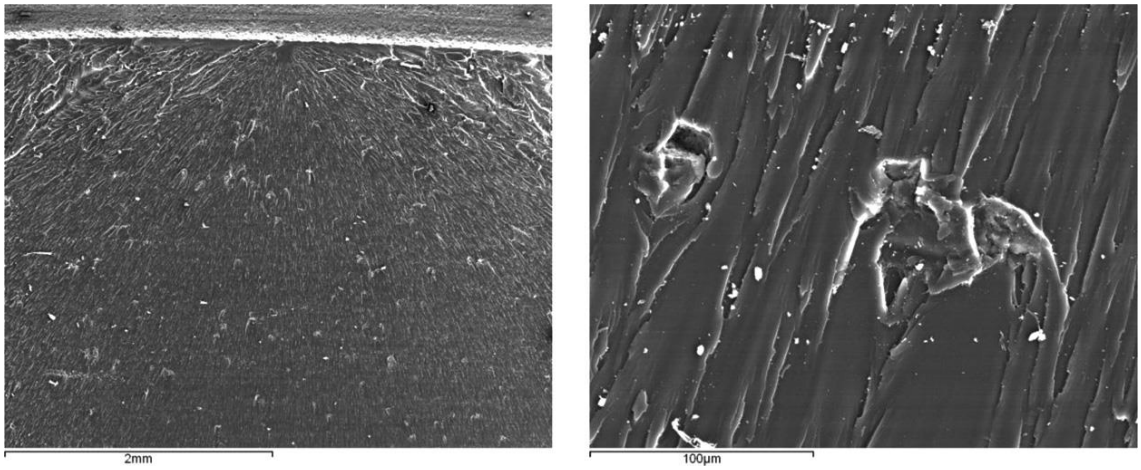


Figure 20 - Fracture surface of a specimen with 5% of untreated cork (38–53 µm). Left— overview of fracture surface; Right—detail of fracture surface.

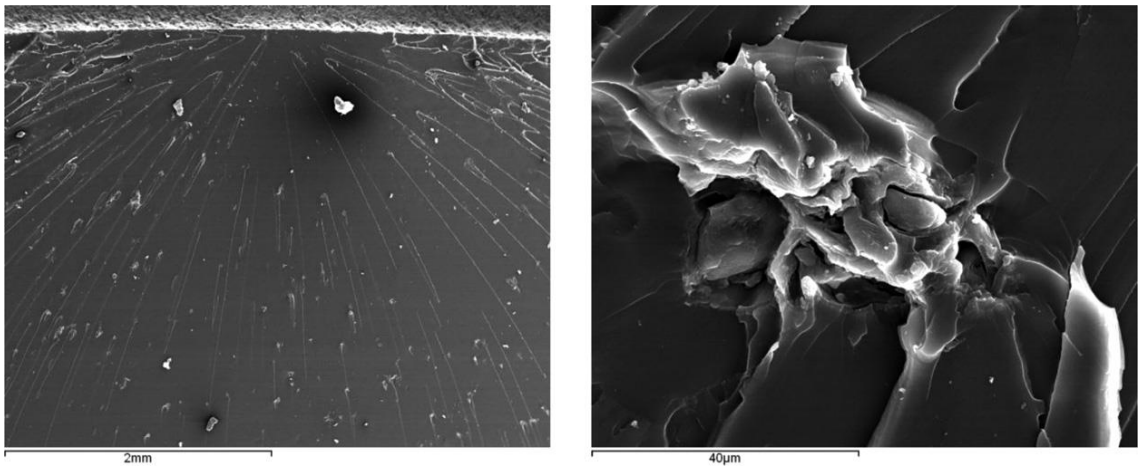


Figure 21 - Fracture surface of a specimen with 5% of treated cork (38–53 µm). Left—overview of fracture surface; Right—detail of fracture surface.

Figures 22 and 23 show the fracture surface of specimens with 1% of cork particles of 125–250 µm size (untreated and treated, respectively). In both figures, it is evident that cork particles are empty inside, promoting energy absorption. These figures show that there are several crack planes close to the cork particles, which indicates that cork is acting like an obstacle to crack propagation.

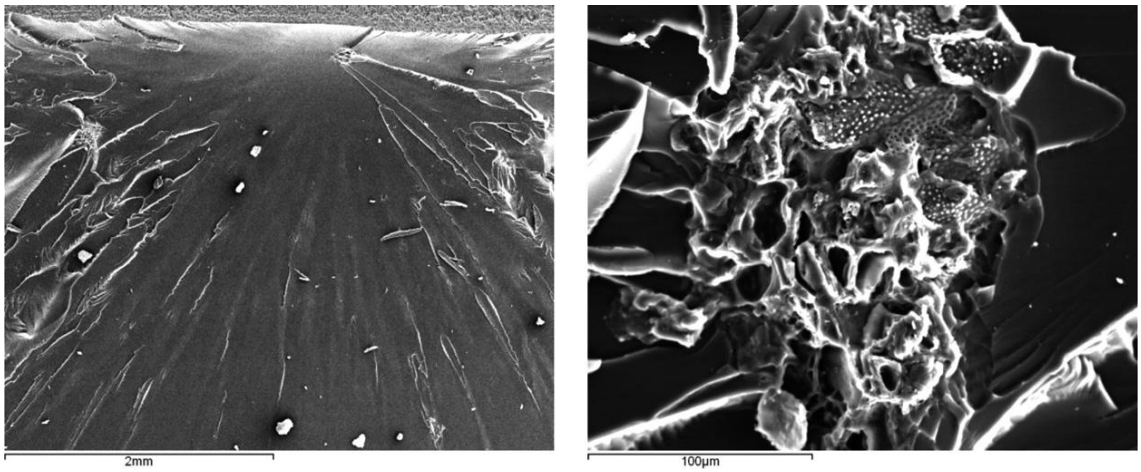


Figure 22 - Fracture surface of a specimen with 1% of untreated cork (125–250 µm). Left—overview of fracture surface; Right—detail of fracture surface.

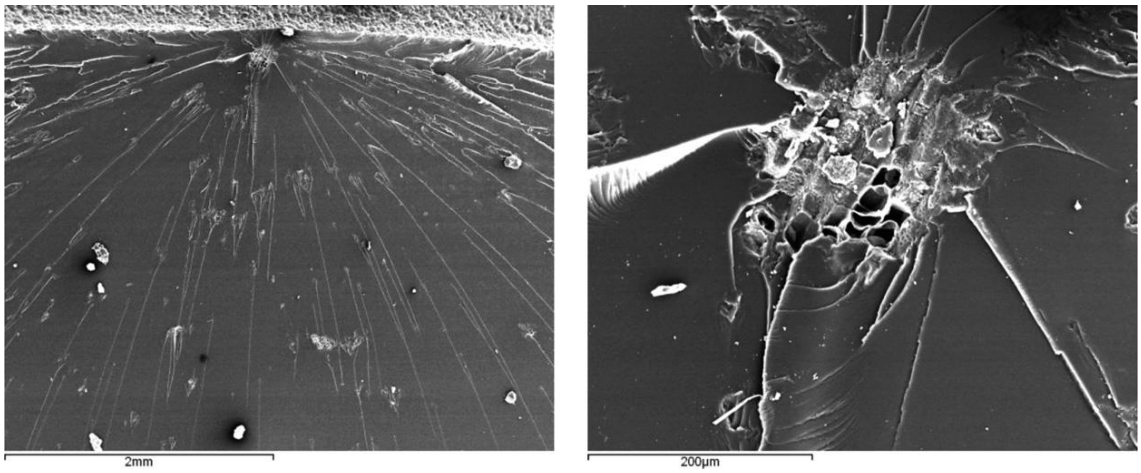


Figure 23 - Fracture surface of a specimen with 1% of treated cork (125–250 µm). Left—Overview of fracture surface; Right—detail of fracture surface.

Figures 24 and 25 show the fracture surface of specimens with 5% of cork particles of 125-250 µm size (treated and untreated, respectively). Figure 24 shows that cork particles are more concentrated in one side. Despite a generally good distribution of particles, when high amounts of cork were included, some agglomeration occurred. Figure 25 (right) shows a cork particle highly compressed: its structural cell is not typical of a cork cell; therefore, this cork particle is not able to absorb the same impact as a cell with an intact structure. Analyzing Figs. 18 to 25, the fracture surfaces show that cork particles vary widely in distribution and disposition in the resin.

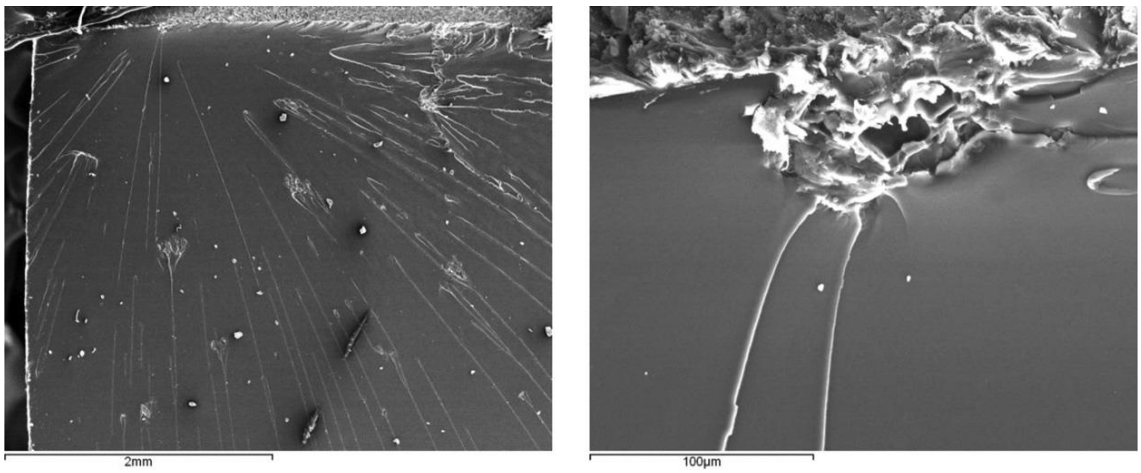


Figure 24 - Fracture surface of a specimen with 5% of untreated cork (125–250 µm). Left—overview of fracture surface; Right—detail of fracture surface.

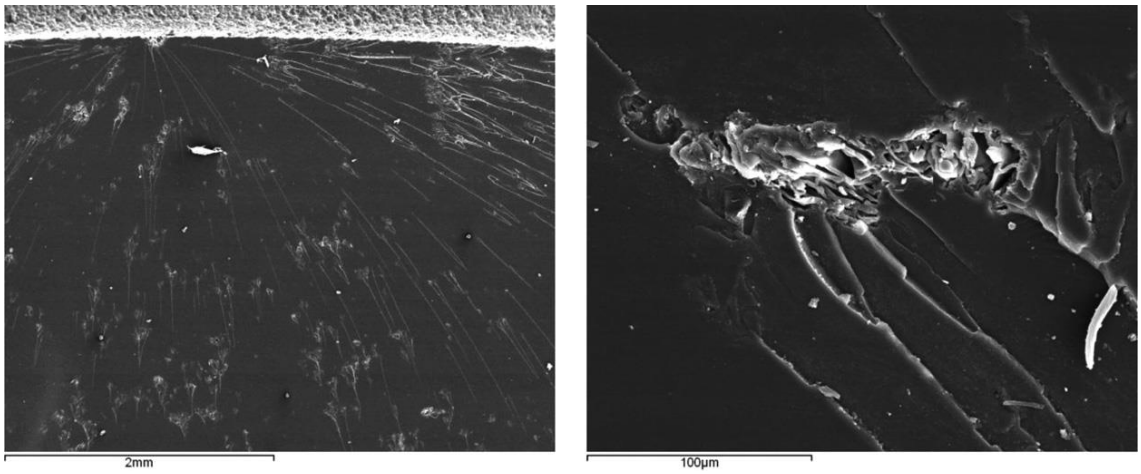


Figure 25 - Fracture surface of a specimen with 5% of treated cork (125–250 µm). Left—overview of fracture surface; Right—detail of fracture surface.

4. CONCLUSIONS

The preliminary tests made of the surface of the cork board showed that: Plasma treatment increases the surface energy of the cork board. However, atmospheric plasma treatment shows a greater increase in the polar component of surface energy. Although atmospheric plasma treatment shows a higher surface energy (compared with untreated cork board and atmospheric plasma treated cork board), it cannot be used on cork particles. For the treatment of cork particles, low pressure plasma must be used to avoid the dispersion of particles in the chamber.

- Low density plasma treatment decreases the contact angle and increases the wettability of cork. There is an erosion of the surface which increased roughness, promoting adhesion between cork and adhesive. In cork particles, this surface treatment must be optimized. Cork wall cells are thin and if the treatment time or the distance of the torch is not the optimal, these walls can be destroyed and adhesive care fill cork cells. In future studies this effect must be analysed.

The influence of the size and amount of cork particles on the impact toughness of a structural brittle adhesive was evaluated by impact tests. The following conclusions can be drawn:

- SEM and OTM analyses show that most cells of the big particles (125–250 µm) are not filled with resin.

- The amount of cork, size of particles, and surface treatments result in different fracture behaviours and morphology.
- Small amounts of cork particles with a structure composed of a limited number of cells (1–5 cells) with well preserved wall cells incorporated in a brittle resin present a better impact energy absorption than large amounts or small particles.

ACKNOWLEDGMENTS

Financial support by Foundation for Science and Technology (PTDC/EMETME/098752=2008) and Professor José Pissarra from the Biology Department from Science Faculty of Porto University are greatly acknowledged. The authors also want to thank Huntsman for supplying the adhesive used—Araldite 2020®.

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Paper 3

Tensile strength, SLJ tests and glass transition temperature measurements

Effect of the amount of cork particles on the strength and glass transition temperature of a structural adhesive

A.Q. Barbosa[1], L.F.M. da Silva[2], A. Öchsner[3]

[1]IDMEC, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

[2] Department of Mechanical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

[3]Faculty of Mechanical Engineering, Universiti Teknologi Malaysia (UTM), 91310 UTM Skudai, Johor, Malaysia

ABSTRACT

The inclusion of particles (micro or nano) is a method to improve the mechanical properties, such as toughness, of structural adhesives. Structural adhesives are known for their high strength and stiffness but also for their low ductility and toughness. There are many processes described in the literature to increase the toughness, being one of the most common the use of rubber particles. In the present study, natural micro particles of cork were used with the objective to increase the ductility of a brittle epoxy adhesive. The idea is for the cork particles to act like a crack stopper. The influence of the cork particle amount was studied. Particles of cork ranging from 125 to 250 μm were mixed in the epoxy adhesive Araldite 2020® from Huntsman. The amount of cork in the adhesive was varied between 0.5 and 5% in weight. This evaluation was made using tensile tests and it was evident that the failure strain was related to the amount of cork particles in the resin. The results concerning the single lap joints and the glass transition temperature confirm the increased ductility obtained in the tensile tests.

Keywords: adhesive, cork, tensile strength, glass transition temperature, single lap joint

1 - INTRODUCTION

One of the most common structural adhesive is the epoxy resin. The densely cross-linked molecular structure of structural adhesives is responsible for the good properties of these materials, but unfortunately it also makes them inherently brittle (low ductility and toughness) with poor resistance to crack propagation [1, 2]. Toughened polymers represent a large area of scientific and technological concern. The problem of polymer toughening emerged in the 70's and since then has experienced a steady increase of interest all over the world. The ability of an adhesive to absorb energy without catastrophic failure can be increased through toughening of adhesives with addition of a second phase. This results in enhanced resistance to fracture and impact with minimal change in the gross properties of the matrix resin [3, 4]. Natural fibers or particles reinforced composites are an emerging area in polymer science. They are gaining attention as reinforcements of polymeric matrices due their unique properties: thermal insulation, low density, low cost, biodegradable, non-abrasive and sustainability of the raw material [4]. Natural fibers themselves are cellulose fiber reinforced materials as they consist of microfibrils in an amorphous matrix of lignin and hemicellulose. These fibers consist of several fibrils that run all along the length of the fiber. The hydrogen bonds and other linkages provide the necessary strength and stiffness to the fibers [5].
Lignocellulosic materials (to which natural material fibres belongs) are among the world´s renewable materials and contribute significantly to word economy. Portugal is leading the world market of this raw material, producing three-quarter of the total production [6]. Cork may be described as a homogeneous tissue of thin-walled cells, regularly arranged without intercellular space. Cork reveals an alveolar structure, similar to a honeycomb, without empty spaces between contiguous cells, which are therefore closed units. This cell configuration confers to the composite the ability to absorb more impact, compared to the brittle resin without particles [7-10].
Cork structural properties could be very useful to reinforce a brittle resin, especially to improve the toughness as the closed cells could work to absorb the impact. However, the properties of a resin/cork composite are not only dependent on the materials properties, but also on their interfacial adhesion properties between the cork and the resin, size and amount of cork particles and mixing conditions [4]. Cork is a material

closed cell with prismatic cells that work together and is a material elastically orthotropic axisymmetric relative to the direction of the tree. The main characteristics of the cork derive from the interaction between cells as a whole (the plate, board or particle board), however it was observed that most of the properties of the cork has the most common forms of use may also be observed in the particles small dimensions. Nevertheless, these particles should have a considerable number of cells, so that they can work together, for example particles of one or two cells no longer have the same mechanical properties as compared to larger particles. Therefore, only a particle with a considerable number of cells may exhibit a damping effect and increase the impact absorption of the resin [11-13]. The properties of the composite depend greatly of phase properties, but also the geometry of dispersed phase (particle size, distribution, orientation) and phase amount. We studied the effect of cork particles on the impact properties of a modified epoxy, and it was concluded that 1% of cork presents better impact absorption, comparing to large amounts (5% of cork particles), for a brittle resin with particles of a characteristic length of 125-250 μm [13].

It is expected that the glass transition temperature (T_g) presents variations with different amounts of cork. Singh et al. [14] made a similar study using rubber particles ($T_g \approx$ - 70°C) as reinforcement material of brittle thermosetting polymers, and concluded that addition of micron rubber particles reduce the elastic modulus and tensile strength and lowers the T_g. Cork presents a T_g values (≈ room temperature, [6]) lower than the brittle epoxy used in this study, so it is expected that cork presents a similar behaviour to rubber, lowering the T_g and elastic modulus.

In this study, different amounts of cork were added to a brittle epoxy to analyse the influence of these particles on the mechanical behaviour of the cork/resin composite. Dog-bone specimens were loaded in tension and single lap shear tests were also carried out to confirm the behaviour of the composite when in a joint. It is well known that the joint strength depends on the adhesive strength and ductility [15]. The effect of the particles on the T_g was measured using a dynamic mechanical analysis type apparatus.

2- EXPERIMENTAL

2.1 - Materials

Cork powder with 125-250 µm size was used. The authors have shown in a previous study that this size corresponds to the best mechanical properties of the composite resin/cork [13]. The cork used was supplied by Amorim Cork Composites (Mozelos, Portugal), without any treatment.

The selected adhesive was Araldite 2020®, from Huntsman Advanced Materials (Pamplona, Spain). This is a two component adhesive (100/30 by weight), low viscosity (150 mPa.s), transparent epoxy adhesive that cures at 100°C, within 15 minutes. The Young's modulus of this adhesive is typically 3100 MPa. This material was selected because it is rather brittle, so the improvements on the tensile strength after the cork particles inclusion can easily be observed.

2.2 – Manufacture of bulk specimens

The incorporation of cellulosic fibres in thermoplastics leads to poor dispersion of the fibres due to strong interfibre hydrogen bonding, which holds the fibres together. Cellulose fibres also tend to aggregate and therefore the fibres do not disperse well in a hydrophobic polymer matrix and thus pose difficulties in achieving a uniform distribution of fibre in the matrix [16]. Particle aggregation is also expected when mixing cork particles in an epoxy resin. Therefore, a homogeneous mixture of the cork powder in the resin must be assured to avoid the introduction of air bubbles and a uniform distribution of particles. The cork was initially mixed with the resin using a centrifuge mixing machine, SpeedMixer DAC 150™ (Hauschild, Hamm, Germany), for 90 seconds at 1500 rpm. Then, cork was mixed with the resin and after that the hardener was added to the mixture. This procedure was the same for the different amounts of the cork.

However, but a sufficiently uniform distribution of the cork particles was not reached, due the low density of the cork particles and the adhesive low viscosity. To force a better particle distribution after the mixing, the composite was heated to 50°C during 15 minutes, to increase the adhesive viscosity. After this procedure, the composite was

mixed again in the centrifuge mixing machine. This procedure permitted to obtain a uniform particle distribution.

After mixing the cork particles with the resin and hardener, the mixture was cast in a pre-heated steel mould. Release agent was applied to the mould to ensure easy release of the bulk specimen. A silicone rubber frame was used to apply a hydrostatic pressure to the adhesive, which was hot pressed (2 MPa) for 15 minutes at 100°C (according to the manufacturer's recommendation cure schedule), as show in Figure 1. Specimens were machined from the plates manufactured with the mould [17].

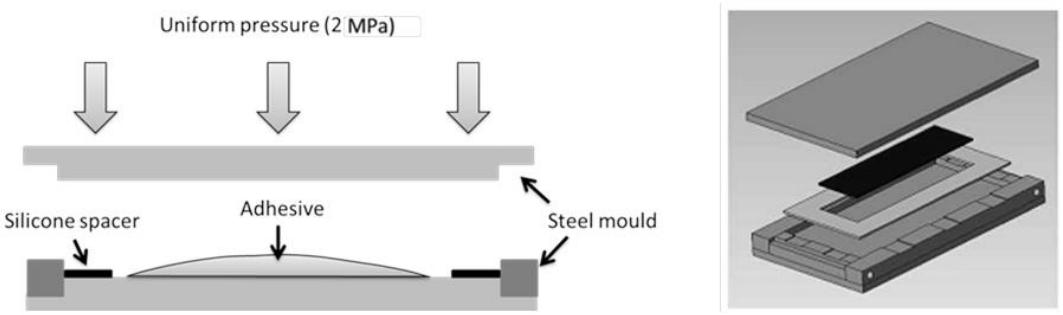

Figure 1- Mould for bulk specimens. Expanded view with steel plates and silicone rubber frame [17].

2.3- Scanning electron microscopy analysis

Scanning electron microscope (SEM) analyses were produced in a JEOL JSM 6301F/ Oxford INCA Energy 350/Gatan Alto 2500 microscope (Tokyo, Japan). This equipment was used to analyse the cork particles, the particles distribution and surface fractures.

2.4 – Tensile tests

Specimens with and without cork, were manufactured, according to the test plan represented in Figure 2.

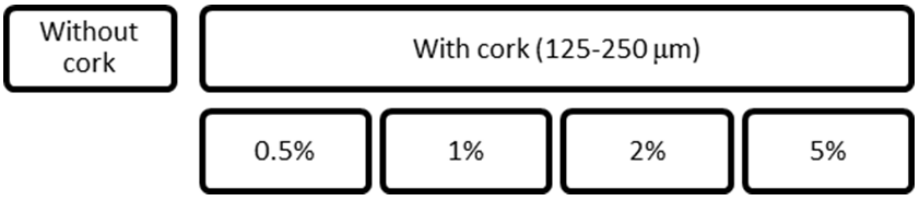

Figure 2 - Schematic diagram of cork specimens with amounts of cork (% in volume).

Tensile test specimens according BS 2782 standard were manufactured. Figure 3 shows the dimensions of machined specimens, with 2 mm of thickness. The tensile tests were carried out in a Instron 3367 universal test machine, with a capacity of 30 kN (Norwood, USA). This test was made at room temperature and test speed of 1 mm/min. Three specimens were tested for each condition.

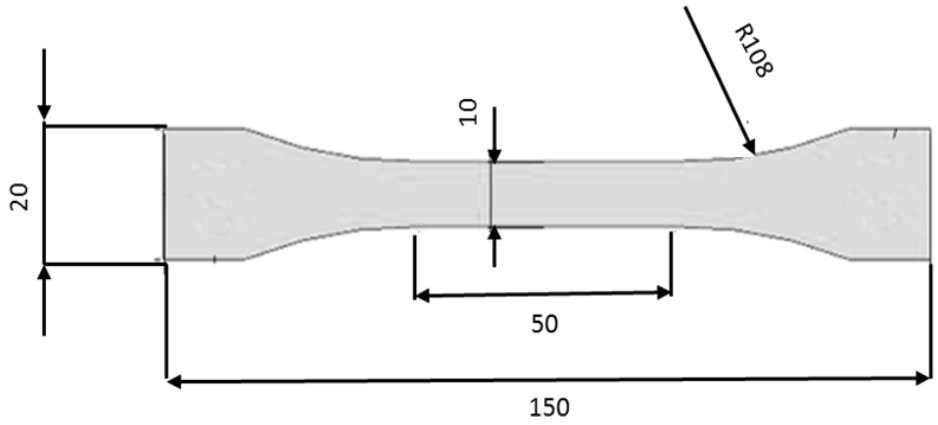

Figure 3 - Dog-bone tensile test specimens (2 mm thickness) according to BS 2782 standard (dimensions in mm).

2.5 – Single lap joint tests

The single lap joints (SLJs) were tested in the same machine as the tensile tests under the same conditions (room temperature and test speed of 1 mm/min). Three specimens were tested for each condition. Specimens with and without cork were manufactured according to the test plan represented in Figure 4. The geometry and dimensions of the SLJs are given in Figure 5. For ductile adhesives, the SLJ strength is proportional to the overlap. Therefore, joints of increasing overlap (12.5, 25 and 50 mm) were tested to check the adhesive ductility. The SLJs were manufactured individually in a mould and the adhesive thickness was controlled by packing shims. High strength steel adherends

were used to guarantee that there is no yielding of the adherends. The adherend selected was a high strength steel (DIN C65 heat treated) with a yield strength of 1260 MPa to avoid plasticity of the adherends.

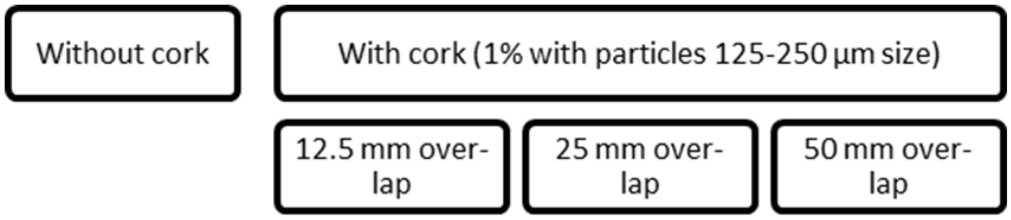

Figure 4 - Schematic diagram of SLJ with amounts of cork (% in volume) and different overlap length.

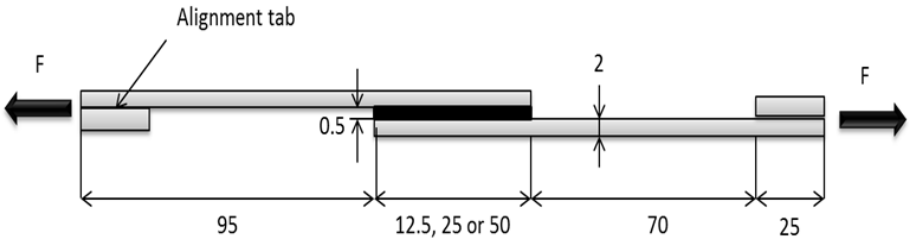

Figure 5 - Single lap joints geometry according to ASTM D 1002 (dimensions in mm).

2.6 – Measurement of glass transition temperature (T_g)

A dynamic mechanical type analysis method initially developed by Adams and co-workers [18] was used to determine the glass transition temperature (T_g) of the composite cork/resin. The method involves excitation of the test specimen during the heating and the cooling. T_g is measured by registering the damping of the specimen as a function of temperature. T_g, in this case is defined as the temperature at which the peak value of damping is observed. The heating rate should be such as to ensure a homogeneous temperature distribution in the specimen. However, it cannot be too high not to cause a post-cure in the specimen. Figure 6 shows a schematic diagram of the rapid method of measuring the T_g.

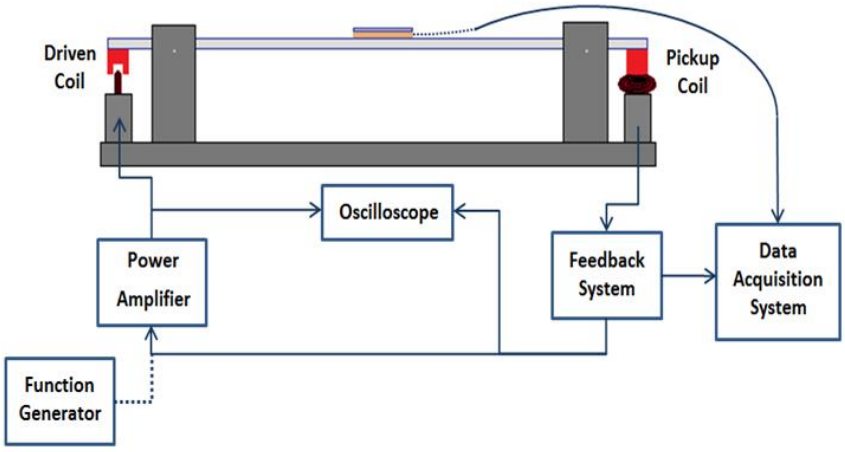

Figure 6 - Schematic diagram of the apparatus used in the testing of the T_g.

The vibration of the specimen is due to a sinusoidal alternating current of known frequency, previously amplified using a power amplifier and sent to the driving coil. The feedback circuit allows maintaining the system at resonant oscillation regardless of variations in the resonant frequency. The variation of temperature (heating and cooling) of the specimen causes changes in properties such as damping, modulus and even geometrical dimensions. As a result, to keep the system vibrating at resonance the frequency of the input signal needs to be constantly adjusted. The feedback unit maintains the oscillation of the specimen at resonance adjusting continuously, ensuring a very quick response to any sudden change in the resonant frequency caused by factors such as temperature. The temperature is not measured directly on the specimen at resonance because by putting the thermocouple wire on it, an extraneous constraint and damping source could lead to a distortion of the results. The technique of reference junction (dummy specimen) is used for monitoring and measuring the temperature. The signal from the dummy specimen is also sent to the data acquisition system in order to record the change of temperature with time. Both graphs (amplitude and temperature as a function of time) can be merged in order to obtain a graph of amplitude as a function of temperature.

The method used to attach the polymer consists in using a pre-cured sheet of the polymer which is attached between the beam and constraining layer by a bolt (see Figure 7).

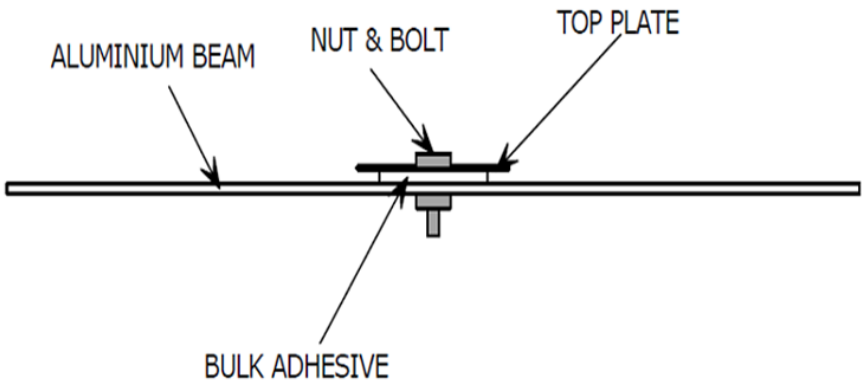

Figure 7 - Schematic representation of the bulk specimen for Tg measurement.

3 -RESULTS AND DISCUSSION

3.1 - Cork particles characterization

The cork particles size and shape were analysed in SEM. Particles with 125-250 µm size have a honeycomb structure composed by several cells, some open (edges of particles), but a few cells are closed (particle core) (see Figure 8).

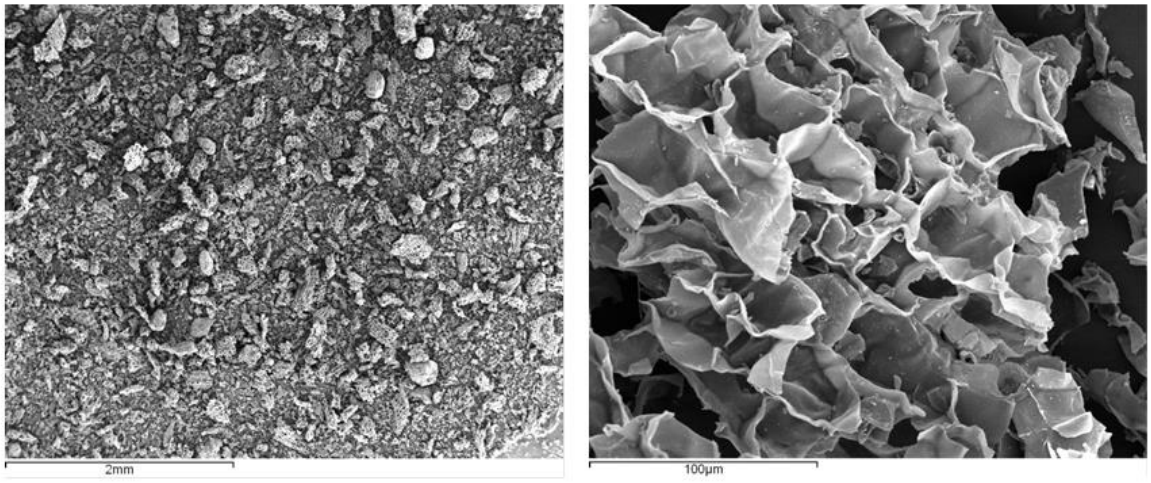

Figure 8- Microstructure of cork powder particles with 125-250 µm size.

The authors of the present paper concluded in a previous study [13] that the number of cells present in a particle is very important for the good impact behaviour of the cork

particles. Due the milling process to obtain cork particles, some cells present damages on the walls. Cork particles with cells wall damage can facilitate the resin penetration which can decrease the damping effect of the cork, decreasing the absorption of energy according to the mechanism presented in Figure 9. The authors concluded that it is crucial that cork particles present a few well preserved cells in the particle based on the mechanical behaviour of large particles (125-250 μm) with well-preserved cells wall against small particles (53-38 μm) with damage cells wall. The large particles presented better results as reinforcement material compared to small particles.

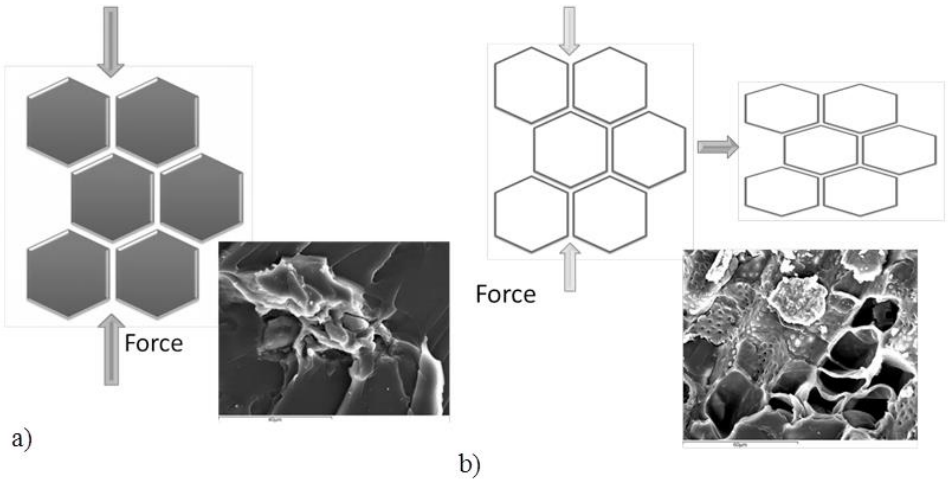

Figure 9 - Schematic representation of the effect of damping of cork cells. (a) cork cell filled with resin; (b) cork cell without resin penetration [13].

3.2 – Cork distribution characterization

Density of cork is lower than epoxy (0.20 g/cm^3 and 1.15 g/cm^3, respectively). The selected epoxy resin is rather liquid. The low viscosity promotes the agglomeration of the cork on the sample surface when the resin cures. Figure 10 shows an overview of fracture surface of a tensile specimen containing 1% of cork cured at 100°C during 15 min without the pre-heating stage described in Section 2.2. It can be seen that the cork particles are mainly found on one of the specimen's surfaces and agglomerated.

Figure 11 presents details of Figure 10, which clearly shows agglomeration of particles of cork. This agglomeration gives mechanical properties very different from those of samples in which the distribution of the cork is random and uniform throughout the sample (see Section 3.3). With agglomeration, the specimens have a very high scattering of results and sometimes do not work with the cork as a reinforcement material but as a defect.

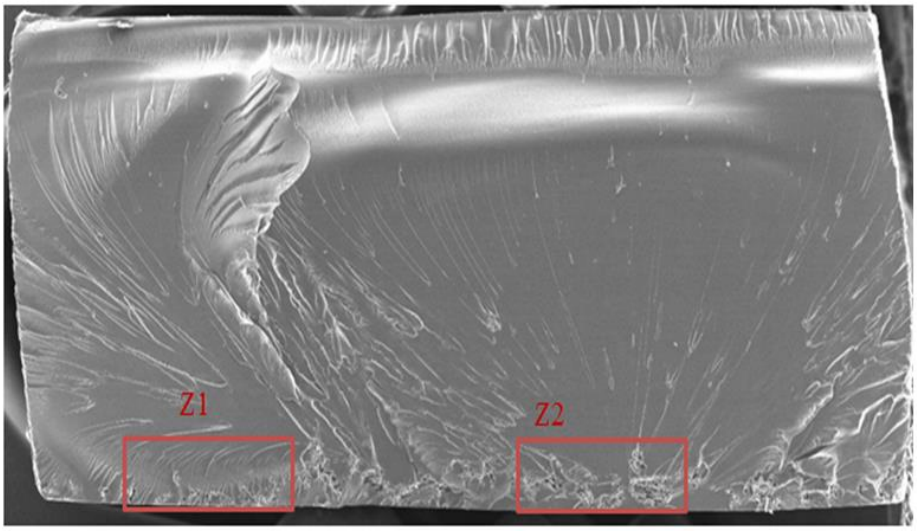

Figure 10 - Cork distribution in a specimen with 1% of cork, on the fracture surface of a tensile specimen manufactured without a pre-heating stage (see Section 2.2). Z1 and Z2 areas shown in Figure 11.

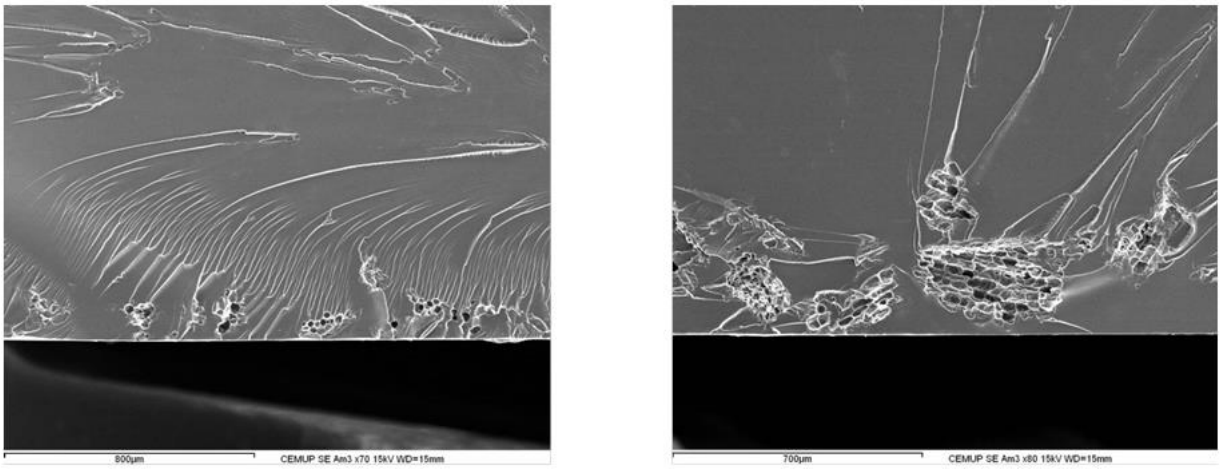

Figure 11 – Left - Zone 1 of Figure 11; Right - Zone 2 of Figure 11.

Pre-heating the resin fostered an increase in viscosity which makes the free movement of the cork particles more difficult. Thus, with the aid of mechanical means of centrifugation, the particles distribution was random and uniformly distributed, without the presence of agglomeration. Figure 12 presents the fracture surface of a specimen with 5% cork with the use of a pre-heating stage. This case corresponds to the case where agglomeration of particles is particular important due to the high quantity of cork to mix. Figure 13 shows that even with a high amount of cork, cork agglomeration is not visible in the specimen.

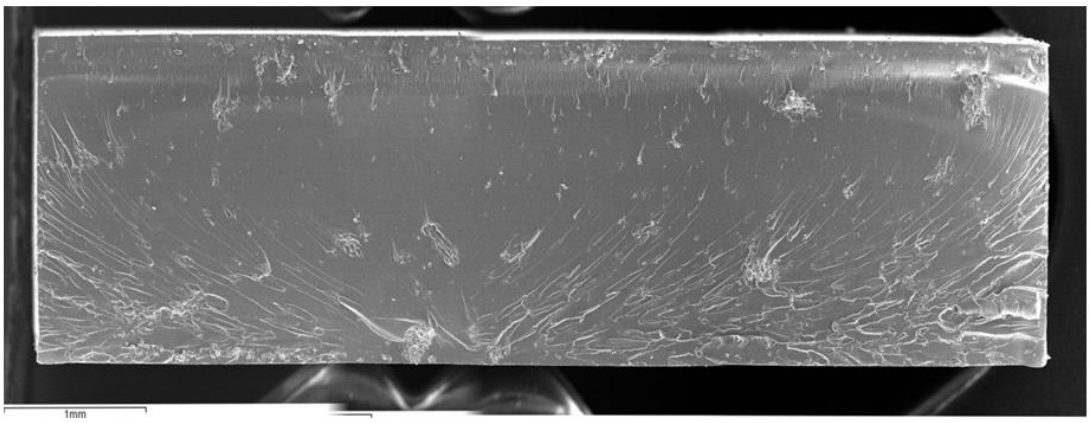

Figure 12 - Cork distribution in a specimen with 5% of cork manufactured with a pre-heating stage (see Section 2.2).

3.3 – Tensile strength tests in specimens without cork – influence of the pre-heating

In order to study the effect of the pre-heating stage on the adhesive properties, tensile tests were carried out with and without pre-heating. The results are presented in Figure 13. It can be concluded that the pre-heating stage does not influence the mechanical behaviour of the epoxy.

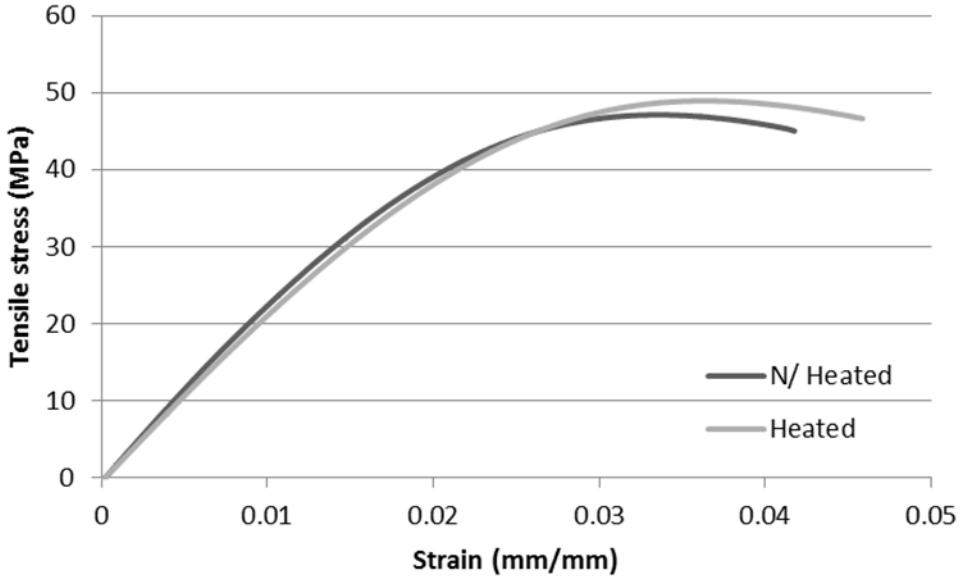

Figure 13 - Tensile stress-strain curves for heated and unheated specimens.

3.4 – Tensile strength properties

Figure 14 shows typical tensile stress-strain curves of the neat epoxy resin and of the epoxy resin with 0.5, 1, 2 and 5% of cork particles. These curves show that cork has little impact on the strength and Young's modulus (see also Figures 15 and 16). However, the effect of cork particles on the adhesive ductility is significant (see Figure 17). Specimens with small amounts of cork (0.5 and 1% of cork) present a higher maximum strain to failure than specimens without cork particles. However, specimens with 2 and 5% cork present a lower value of strain. There seems to be an optimum amount of cork particles for obtaining the best adhesive ductility. Below 1% of cork, the amount is insignificant and above 1% the cork particles start to act as defects since the adhesive becomes more brittle.

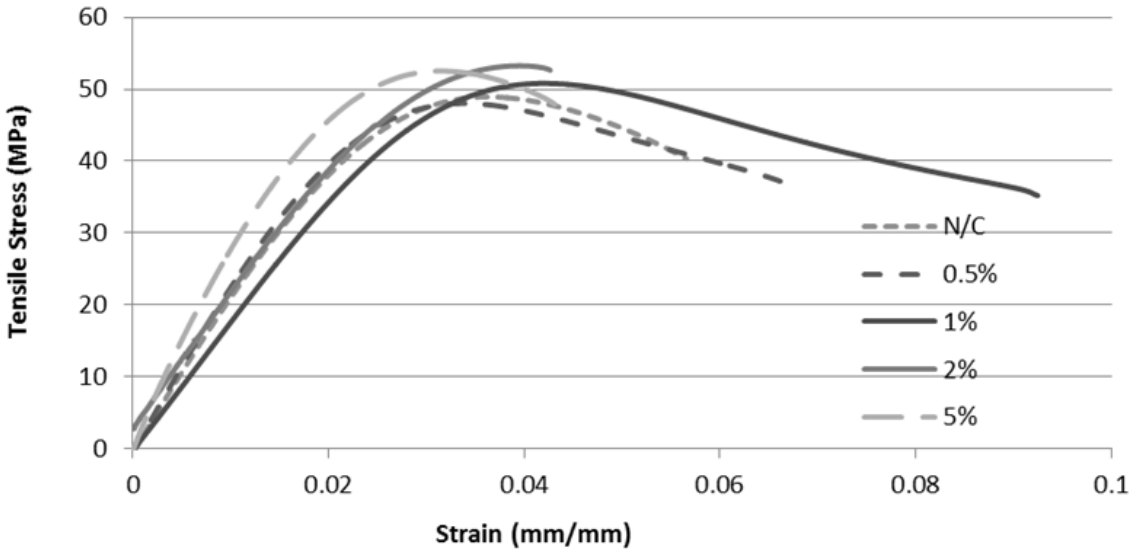

Figure 14 – Tensile stress-strain curve of specimens with different cork amounts (n/ cork, 0.5, 1, 2 and 5%).

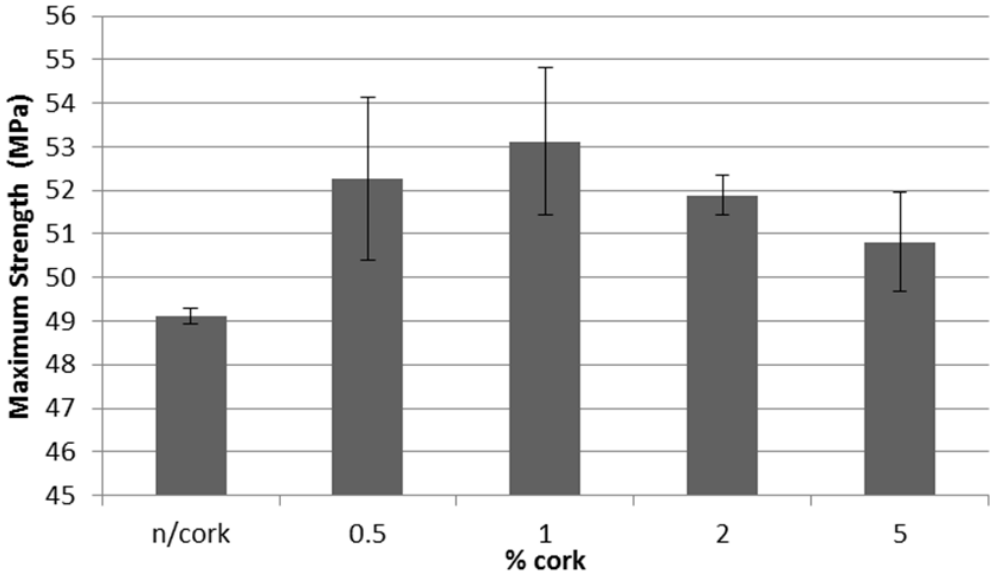

Figure 15 - Maximum strength of specimens with different cork amounts (n/ cork, 0.5, 1, 2 and 5%).

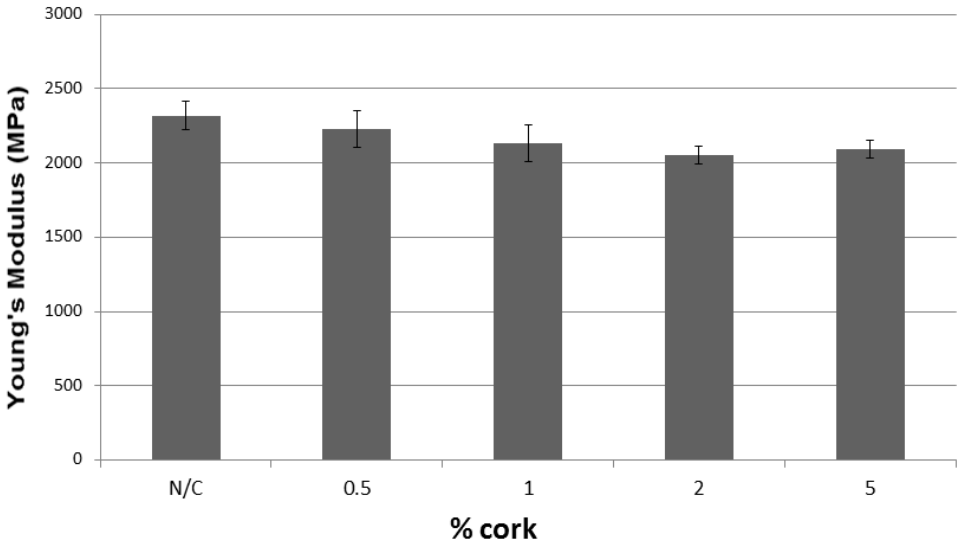

Figure 16 - Young´s modulus of specimens with different cork amounts (n/ cork, 0.5, 1, 2 and 5%).

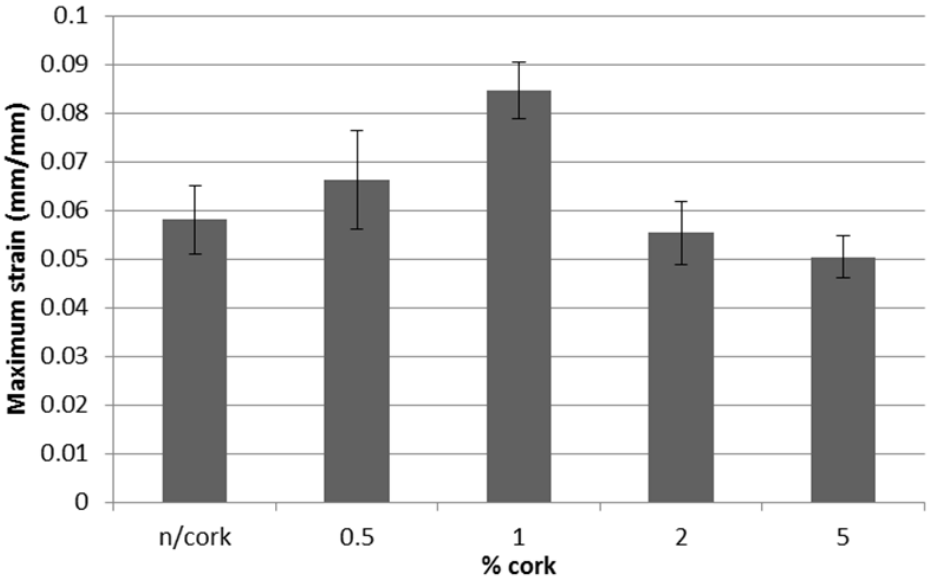

Figure 17 - Maximum strain of specimens with different cork amounts (n/ cork, 0.5, 1, 2 and 5%).

3.5 – Single lap joint tests

In order to confirm the tensile test results, SLJs were tested varying the overlap length. For ductile adhesives (more than 20% of deformation in shear), the joint failure load is proportional to the overlap [15]. The adhesive has yield strength of approximately 40 MPa with or without cork particles (see Figure 14). Supposing that the adhesive follows

the yielding criterion of von Mises, the shear yielding strength is approximately 25 MPa. Figure 18 shows the failure load of the SLJs as a function of the overlap length for specimens without cork and 1% cork. A line corresponding the global yielding of the adhesive is also shown, corresponding to the following equation:

$$P_{GY} = \tau_Y . b . l \quad (1)$$

where P_{GY} is the failure load of the adhesive due to global yielding, τy is the yield strength of the adhesive, b is the joint width and l is the overlap length. That criterion assumes that the joint fails when the whole adhesive overlap has yielded and gives good predictions when the adhesive is ductile (more than 20% in shear). In that case the failure load is proportional to the overlap. For 12.5 mm overlap, the strength of the joints with and without cork is similar and close to the global yielding line. For short overlaps, the adhesive stress distribution is rather uniform and a small amount of adhesive ductility is sufficient to yield globally the overlap. For 25 mm overlap, the joint strength values are again similar but deviating from the global yielding line. That means that the joint fails before the adhesive yields completely along the overlap. For 50 mm overlap, there is a clear distinction between the joints with and without cork. Joints with cork give a much higher failure load, indicating that more of the adhesive overlap has yielded in the case of the joint with cork particles. This is a clear indication that the adhesive with 1% cork particles has a more ductile behaviour than the neat epoxy resin. Bearing in mind the ductility of the adhesive modified with 1% cork particles (nearly 10% strain to failure in tension, see Figure 17, one would expect the experimental joint strength to be closer to the global yielding point. However, it has been shown before by Grant et al. [20] that the global yield criterion is not adequate for thick bondlines, as is the case in the present study. The global yield criterion overestimates the results of thick bondlines.

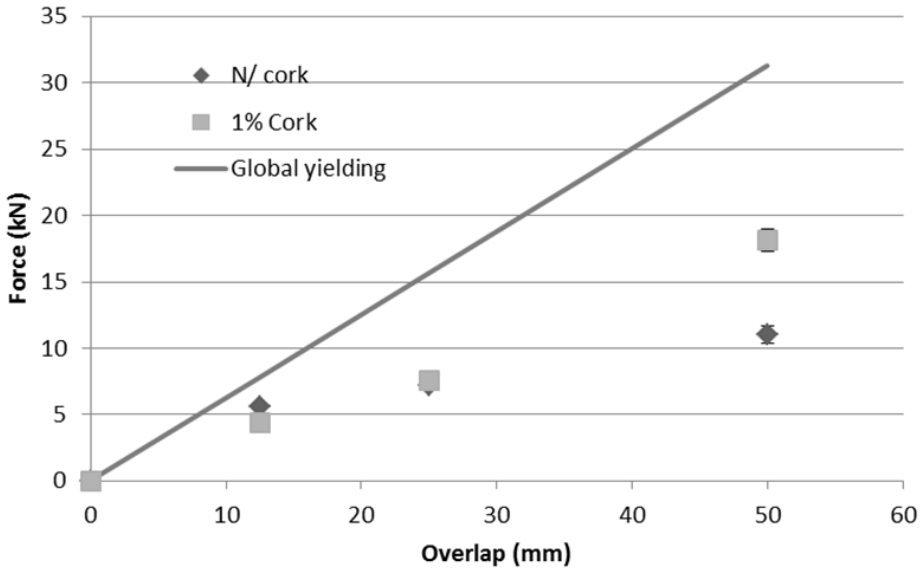

Figure 18 – Failure load as a function of overlap length for SLJs with and without cork.

The fracture surfaces of the SLJs were analysed in SEM and are presented in Figure 19 for the case of a joint without cork particles and in Figure 20 in the case of a joint with cork particles. Figure 19 shows a very smooth fracture surface indicating a brittle behaviour. On the other hand, Figure 20 shows that the fracture surface has multiple crack paths due to the interaction of the crack with the cork particles (Figure 20b) indicating a more ductile behaviour. These figures support the failure load results presented in Figure 18.

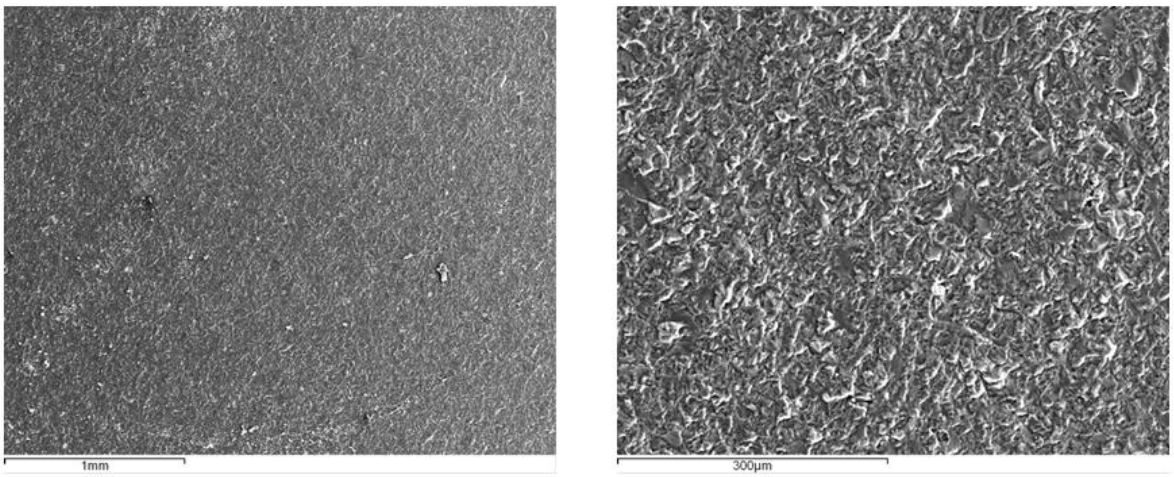

Figure 19 - SLJ fracture surface of a specimen without cork. a) surface overview; b) surface detail.

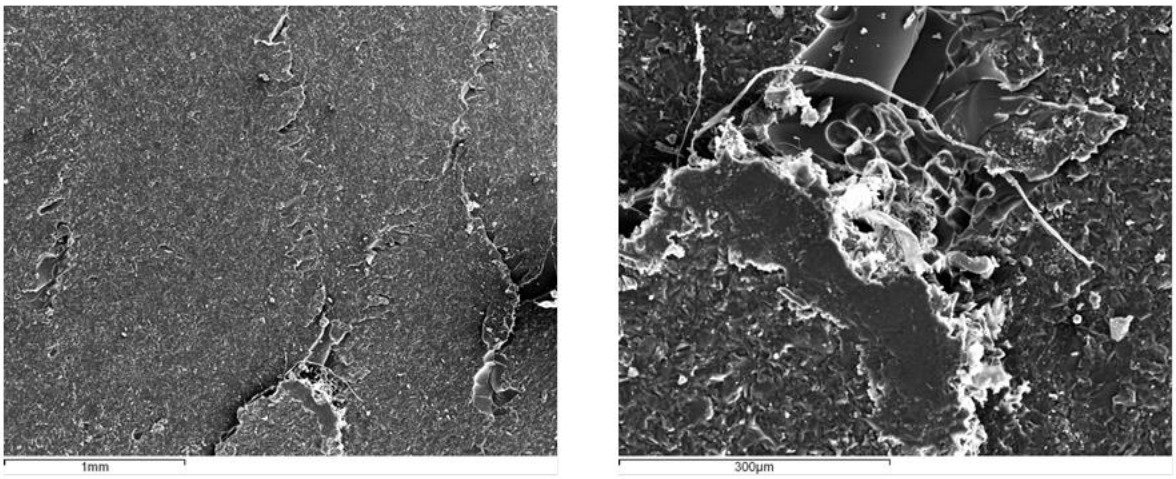

Figure 20 - SLJ fracture surface of a specimen with 1% cork. a) surface overview; b) surface detail, with a cork particle on a crack.

3.6 – Glass temperature transition measurements

According to Fortes et al. [6], since the cork cellular wall is essentially a polymer, cork has a T_g, at which mechanical properties undergo significant changes. Some authors suggest that this transition occurs near room temperature. Tests on the cork itself were carried out on cork board specimens and this value was confirmed with a T_g of 16.5ºC.

Figure 21 shows a typical curve damping vs. temperature obtained when measuring the T_g for a sample with no cork particles. The value of T_g was obtained by the maximum value of the damping of the specimen.

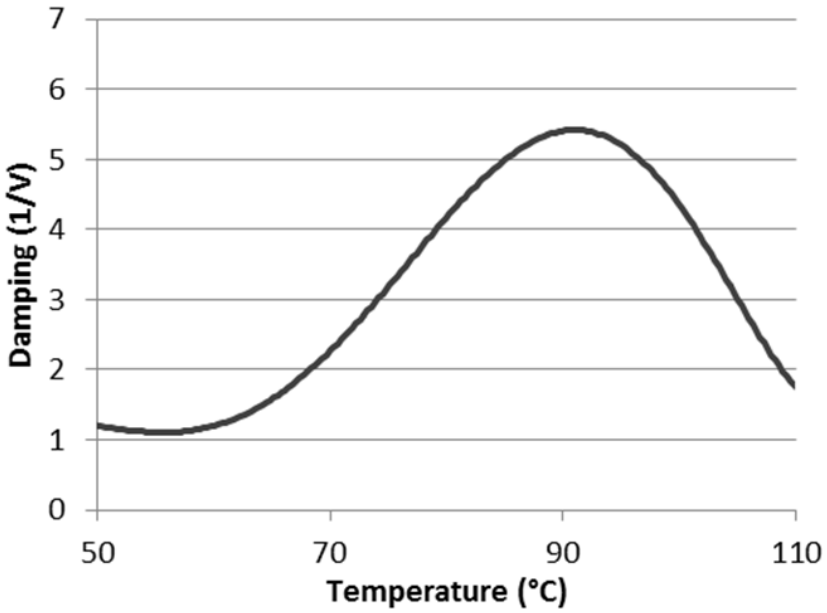

Figure 21 - Curve obtained in the measurement of glass transition temperature for a sample without cork particles.

Figure 22 shows the measurements of T_g of specimens with different amounts of cork (0.5, 1, 2 and 5%). Cork's T_g is lower than the epoxy resin (16.5°C against 87.5°C). Specimens with cork particles present a lower T_g compared with specimens without cork. The same effect occurs when rubber particles are added as reinforcing material in fragile epoxies, presenting a lowering of T_g values [14]. However, there is a slight increase in T_g from 1% to 5% cork particles which might be explained by an a decrease of the free volume of the adhesive due to a higher interaction of the adhesive with the cork particles for larger amounts of particles. Nevertheless, more research is needed on this issue so that it can be answered conclusively. The T_g values obtained for specimens with cork particles are in line with the tensile test results. It is known that as the T_g decreases, there is an increase in the ductility of the adhesive [19]. Therefore, the composite which has the lowest T_g (1% of cork) should give the highest ductility, which is consistent with in the tensile tests results.

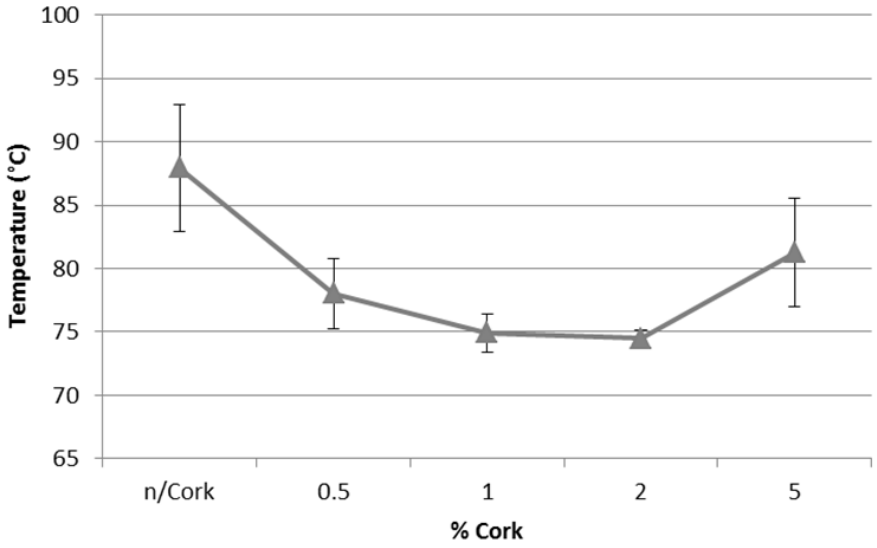

Figure 22 – Glass transition temperature (T_g) measurements of specimens with different cork amounts (n/ cork, 0.5, 1, 2 and 5%).

4 - CONCLUSIONS

The influence of the amount of cork particles on the tensile strength of a structural brittle adhesive was evaluated by tensile strength, SLJ tests and T_g measurements. The following conclusions can be drawn:

- A morphological analysis of the cork particles shows that the particles selected have a few closed cells, which should promote an increased toughness of the material according to the theory proposed previously by the authors in [13].
- 1% of cork particles with a structure composed by a limited number of cells with well-preserved cell walls incorporated in brittle resin give more ductility than other amounts of cork. Specimens above 2% of cork present a worse behaviour than specimens without cork probably because from that point cork particles act like a defect.
- The SLJs results show that joints with 1% of cork have a higher joint strength explained by a higher adhesive ductility, which reinforces the tensile test findings.
- T_g measurements are consistent with tensile tests, showing that specimens with 1% cork have a lower T_g which corresponds to a more ductile behaviour.

ACKNOWLEDGEMENTS

Financial support by Foundation for Science and Technology (PTDC/EME-TME/098752/2008) is greatly acknowledged.

The authors also want to thanks Amorim Cork Composite (Mozelos, Portugal) for supplying the cork powder used.

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Paper 4

Kinetic analysis

Kinetic analysis and characterization of an epoxy/cork adhesive

A.Q. Barbosa [a], L.F.M. da Silva [b], J. Abenojar [c,*], J.C. del Real [d], R.M.M. Paiva [e], A. Öchsner [f]

[a] INEGI, Rua Dr. Roberto Frias 400, 4200-465 Porto, Portugal

[b] Department of Mechanical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias 400, 4200-465 Porto, Portugal

[c] Department of Materials Science and Engineering, Universidad Carlos III of Madrid, Av. Universidad, 30, 28911 Leganes, Spain

[d] Department of Mechanical Engineering/IIT, Universidad Pontificia Comillas, C/Alberto Aguilera 23, 28015 Madrid, Spain

[e] CIPADE–Indústria e Investigação de Produtos Adesivos, S.A., Avenida 1 de Maio, 518, 3701-909 São João da Madeira, Portugal

[f] Griffith School of Engineering, Griffith University (Gold Coast Campus), Building G39 Room 2.22, Parklands Drive, Southport, Queensland 4214, Australia

ABSTRACT

Epoxy resins are the most common structural adhesives due to their good mechanical, thermal and chemical properties. However, the structure of these thermoset polymers, due to the high crosslinking, also causes brittleness, with a low resistance to the initiation of cracks and their propagation. The inclusion of particles (nano or micro) is a common method to improve the mechanical properties such as toughness of structural adhesives. In the present study, natural micro particles of cork were used to increase the toughness of a brittle epoxy adhesive. The main objective of this research was to investigate the effect of the amount of cork particles in the cure reaction of a brittle epoxy, knowing that the amount present influences the mechanical properties. This study was developed using specimens with 0.5, 1, 2 and 5% (volume) of cork and without cork, as reinforcement material of a brittle resin. In general the cork particles do not influence the curing process, although they slightly change the curing mechanism. Also, cork particles decrease the glass transition temperature (T_g) and have a plasticizer effect in the epoxy resin.

Keywords: Thermosetting resin, Curing process, Kinetics, Cork micro-particles, Differential scanning calorimetry

1. Introduction

One of the most common structural adhesive is the epoxy resin, due to its good mechanical, thermal, adhesion and chemical properties. The densely cross-linked molecular structure of structural adhesives is responsible for the good properties of these materials, but unfortunately it also makes them inherently brittle (low ductility and toughness) with poor resistance to crack propagation [1,2]. Epoxy resins are the most important thermosetting polymers widely used as matrices in reinforcement composites. Most of the commercially available are oligomers of diglycidyl ether of bisphenol (DGEBA) [3,4]. Polymer composites, such as brittle resins with micro cork particles [5,6], are made of reinforcing particles in an embedded brittle epoxy matrix. However, the ratio between particles/epoxy and the effect of the interface present a major influence on the mechanical behaviour of the composite and on the cure conditions [7]. The effect of particles in the curing process of an adhesive will vary according to the nature of these same particles. There are studies showing that the addition of boron carbide particles in an adhesive does not affect the degree of conversion. However, the particles can act as an accelerator or retarder of the reaction [8]. Erdogan et al. [4] studied the same effect with zeolite particles and concluded that the cure rate was increased by the addition of zeolite. Zeolite particles act as catalyst for epoxy systems. Zuiderduin et al. studied the toughening of polypropylene with calcium carbonate particles and concluded that $CaCO_3$ particles do not act as a nucleating agent in polypropylene since the crystallinity is not increased [8]. Also, Abenojar et al. studied the boron effect in low density polyethylene [9]. In this case the crystallinity and melting temperature increase with boron content. It is well known by the scientific community that the physical properties of cured epoxy resins depend on the structure [10,11], time and temperature of cure [12–15]. Therefore, it is of major interest to know and understand the relationship between the mechanical properties and the structure network, in order to obtain composites with high performance application [3,5,16,17]. The curing of epoxy resins involves the transformation of monomers or pre-polymers with low molecular weight into 3D structure networks. In the polymer curing process, the glass transition temperature (T_g) of the material increases as a consequence of the increases in the cross-linking density [6]. T_g is a very important property of an adhesive,

and is very useful to make the link between the mechanical properties and the cure process. There are several methods to analyse the cure kinetics of epoxies, such a magnetic resonance spectroscopy (NMR) and high pressure liquid chromatography (HPLC) [18–20], Fourier transform infrared spectroscopy (FTIR) [20], and in special differential scanning calorimetry (DSC) [21–24]. The main objective of this research was to investigate the effect of the amount of cork particles in the cure reaction and thermal properties of a brittle structural adhesive. Since, besides changing the mechanical properties of the resin, the cork could modify the crosslinking process and curing mechanism. Also the amount of cork added to the resin could. This study was developed using specimens with 0.5, 1, 2 and 5% (volume) of cork and without cork, as reinforcement material of a brittle resin. The curing process was achieved using DSC and FTIR measurements. The mechanical properties of the modified epoxy were carried out by tensile test.

2. Experimental procedure

2.1. Materials

The selected adhesive was Araldite 2020®, from Huntsman Advanced Materials (Pamplona, Spain). This is a two component adhesive (100/30 by weight), low viscosity (150 mPa s), transparent epoxy adhesive that cures at 100 °C, within 15 min. Component A, the epoxy resin, is composed by diglycidyl ether of bisphenol A, (DGEBA) and diglyciddyl ether of 1,4-butanediol (DGEBOH). On the other hand, component B (hardener) is composed by isophorone diamine (IPDA) Cork powder with 125–250 μm size was used. The cork used was supplied by Amorim Cork Composites (Mozelos, Portugal), without any treatment. Specimens with different amount of cork particles (neat, 0.5, 1, 2 and 5% in volume) were manufactured. The cork was initially mixed with the resin using a centrifuge mixing machine, SpeedMixer DAC 150TM by Hauschild Engineering (Hamm, Germany), for 90 s at 1500 rpm. Then, cork was mixed with the resin and after that, the hardener was added to the mixture. This procedure was the same for the different amounts of the cork. However, a sufficiently uniform distribution of the cork particles was not reached, due the low density of the cork particles and the adhesive low viscosity. In order to obtain a better particle distribution after mixing, the

composite was heated to 50 °C during 15 min, to increase the adhesive viscosity. After this procedure, the composite was mixed again in the centrifuge mixing machine. This procedure permitted to obtain a uniform particle distribution. After mixing the cork particles with the resin and hardener, the mixture was cast in a pre-heated steel mould. Release agent was applied to the mould to ensure easy release of the bulk specimen. A silicone rubber frame was used to apply a hydrostatic pressure to the adhesive, which was hot pressed (2 MPa) for 15 min at 100 °C (according to the manufacturer's recommendation cure schedule [25]). Specimens were machined from the plates manufactured with the mould. This manufacturing technique was used to produce the specimens used for FTIR and DSC (cured specimens).

2.2. Differential scanning calorimetry (DSC)

To analyse the cure kinetics of specimens with and without cork particles a DSC machine supplied by Mettler Toledo GmbH (Greifensee, Switzerland) was used. Aluminium crucibles of 40 ml, with around 7.5 mg of the composite or neat resin for each test were used. Nitrogen was used as purge gas, at 80 ml/min. Isothermal tests of 30 min, at different temperatures (70, 85 and 100 °C), were chosen; a second segment of dynamic scanning from the isothermal temperature to 200 °C at a scan rate of 5 °C/min was added. This way the total heat of reaction was calculated. Two tests were performed for each condition. Non-isothermal (dynamic) tests were also carried out at different heating rates (5, 10 and 2°C/min) from 0 at 200 °C.

2.2.1. Operational method

Three methods were compared in the study of the kinetics and the activation energy of the curing reactions. The evaluation of the kinetic parameters was carried out by the empiric method. Through the isothermal DSC curves of curing, it is possible obtain the reaction rate curves. Thereafter, the experimental data were adjusted to a model for heterogeneous reactions, using kinetic equations called autocatalytic or n-order. The autocatalytic mechanism is characterized by a maximum reaction rate at about 30–40% reaction curing progress. In these models, the kinetic parameters do not have

physicochemical interpretation in many cases and are fitting parameters. For the calculation of the kinetic parameters, the Kamal's method was used [26], according to Eq. (1) where the two mechanisms are included:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \quad (1)$$

In this equation, α and t represent the conversion degree and time, respectively; n and m represent the reaction order and the total reaction order is the sum of them; k_1 and k_2 are the rate constants of the n-order and autocatalytic reaction, respectively [27]. Taking into account that two mechanisms were considered, two rate constants were obtained. In the stages where the chemical kinetics controls the reaction, the rate constants show an Arrhenius type dependence with temperature, as shown in Eq. (2).

$$K = Ae^{-\frac{Ea}{RT}} \quad (2)$$

The kinetics parameters of the curing process can also be examined with isoconversional methods utilizing other empiric models such as those of Flynn–Wall–Ozawa and Friedman used by Zhao et al. [28] in a study of epoxy novolac resin and modified with methanol etherified amino resin. Each model requires different representations and equations, but in all of them at the end an activation energy of the process is obtained. In the present study, the method of Kamal was chosen to have information on the autocatalytic mechanism of the curing reaction. With non-isothermal (dynamic) tests, the reaction kinetic can also be calculated. The model free kinetic (MFK) [29,30] was used. MFK is based on at least three temperature scans at different rates. This option gives reliable predictions about conversions of reactions under simulated conditions and delivers an activation energy which depends on the degree of conversion. In this study, STARe Software of Mettler Toledo GmbH (Greifensee, Switzerland) was used. The model-free methodology has long proved useful to obtain reliable kinetic information on many different processes. The fundamental assumption of the model-free method is that the reaction model f(a) is not dependent on temperature or heating rate. MFK can

be used for epoxy [31] and phenolic resins [32], in curing and degradation processes [33], and in isothermal and nonisothermal curing processes [32,34]. Other empirical models can be used for dynamic kinetic studies such as Kissinger and Flynn–Wall–Ozawa models. For example, Wang et al. [35] used these models for the kinetic study of nanocomposites of carboxyl-modified multi-walled carbon nanotubes/epoxy.

2.2.2. Measurement of the glass transition temperature (T_g)

T_g measurements were carried out by use of a Mettler Toledo GmbH apparatus T_g /DSC (Greifensee, Switzerland). A heat rate of 10 °C/min and 6 mg of composite or neat resin were used, from -20 °C to 200 °C. Two tests were performed for each condition. Scanning was performed twice on each material to determine the thermal history of the material and the data derived from the second scanning curve. The temperature chosen to compare materials was the midpoint. The T_g measurements make it possible, a correlation between the mechanical properties to the thermal and chemical properties.

In many studies, it is very interesting to determine Tg values along with the conversion degree. For this calculation it is necessary to determine the T_{g0} and T_{g1}, values of T_g for resin without hardener (α = 0) and maximum curing (α = 1) respectively. In addition, the heat capacities (ΔCp) (measured in the step curve in the T_g zone) was calculated. A heat rate of 10 °C/min and 6 mg of composite or neat resin were used, from -85 °C to 50 °C for T_{g0}, with a dwell at -85 °C during 15 min for the temperature to stabilize. The T_{g1} was calculated from the first scanning curve of the test performed for calculating T_g. The DiBenedetto equation (Eq. (3)) [36] relates conversion degree of the resin with T_g.

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1-(1-\lambda)\alpha} \quad (3)$$

where α is the conversion degree and λ is a parameter that change between 0 and 1 according to Eq. (4)

$$\lambda = \frac{\Delta C_{p\infty}}{\Delta C_{p0}} \quad (4)$$

2.3. Fourier transforms infrared spectroscopy (FTIR)

FTIR measurements were carried out by a PerkinElmer Spectrum Two apparatus (Waltham, USA). A wave length of (4000–600) cm^{-1} and 0.2 cm^{-1} of scanning velocity were used. These tests were carried out with a $LiTaO_3$ detector (15,700–370 cm^{-1}) and a KBr window. Two tests were performed for each condition. The Spectrum 10 PerkinElmer software Spectrum (Waltham, USA) was used for the data analyses. In these analyses, two types of specimens were used: cured and not cured. A bulk adhesive plate was used to study the chemical properties of the cured samples, as already mentioned above (in Section 2.1). For uncured samples, the resin/hardener was mixed with cork particles, and tested immediately after.

2.4. Tensile tests

Tensile test specimens with and without cork were manufactured according to the specimen geometry defined in ISO 527-2 standard [37]. The tensile tests were carried out in an Instron 3367 universal testing machine (Norwood, USA), with a capacity of 30 kN. This test was made at room temperature and at a test speed of 1 mm/min. Three specimens were tested for each condition. Tensile tests were performed in order to correlate the mechanical properties of materials with the thermal and chemical properties. Generally there is a relationship between these properties.

3. Results and discussion

3.1. Kinetic modelling of cure reaction

3.1.1. Isothermal model

The conversion degree (α) was computed using Eq. (5) [7,26,27,29], where ΔH_t is the reaction heat value for a given time, $\Delta H_{isothermic}$ is the heat value of the isothermal reaction and $\Delta H_{residual}$ is the residual heat of the reaction.

$$\alpha = \frac{\Delta H_t}{\Delta H_{isothermic} - \Delta H_{residual}} \quad (5)$$

Fig. 1 represents the conversion degree (α) versus time for specimens without cork. The calculation of a follows Eq. (5), and as expected, it can be observed that α increases with time and temperature under isothermal curing conditions. Initially, the cure rate is high and then tends to stabilize, for all temperatures. At 100 °C total conversion is obtained in the time studied. The final stage of the cure increases with temperature due to the effect of the diffusion-controlled phenomenon and the functional groups constrained mobility that come in close contact to react [26,27].

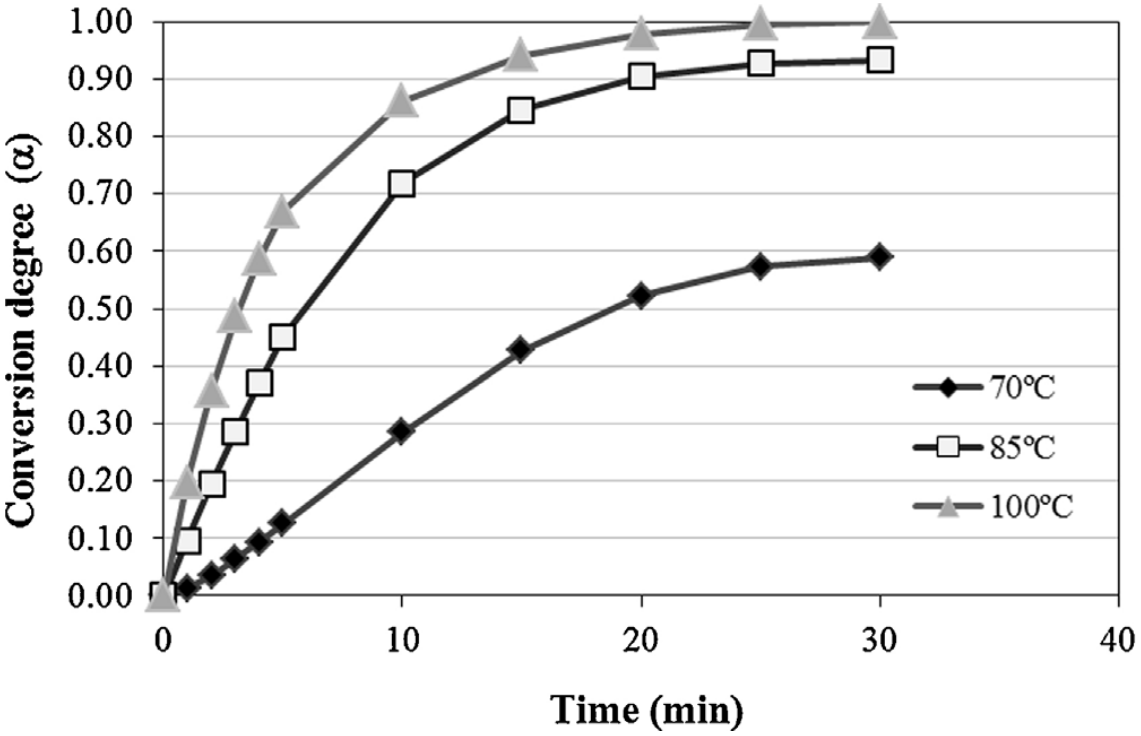

Fig. 1. Conversion degree (α) for neat resin at different temperatures (70, 85 and 100 °C).

Analysing Fig. 2, it is observed that the temperature at which the adhesive cures has a greater influence on the conversion degree. At a temperature of 100 °C the adhesive is fully cured at 30 min, temperature at which the material is cured for tensile tests, FTIR analysis and T_g. On the other hand, the cork particles amount does not show any significant influence on the conversion n degree. In contrast to what is common in the presence of reinforcement particles [4,7,8,27], the presence of cork does not delay the reaction but neither activate the reaction. At 85 °C, the neat resin and the composites have a conversion degree between 0.85 and 0.93; the lowest value is for the composite

with 1% cork and the highest value for the composite with 5% cork. These differences could be important if it is assumed that the material could be cured at 85 °C, because for the same time a higher degree of conversion is obtained. When the isothermal test is carried out at 70 °C, a increases with the amount cork, except for 5%, where the same value is maintained (Fig. 2). At this temperature, the autocatalytic mechanism has more importance and the cork particles could be the catalysing process, having a similar behaviour to the OH groups. The cork composition is suberin, lignin (soluble and insoluble) and polysaccharides. Polysaccharides are dehydrated at 70 °C as many organic compounds. In this case the cork is in the epoxy resin, where OH groups are formed. If the cork is effectively dehydrated, it is releasing water (OH^- + H^+), and these OH can have a catalytic effect similar to the OH of the oxirane ring. When 5% cork particles are added, the autocatalytic and steric impediment effects might be competing, for this reason curing degree is lower

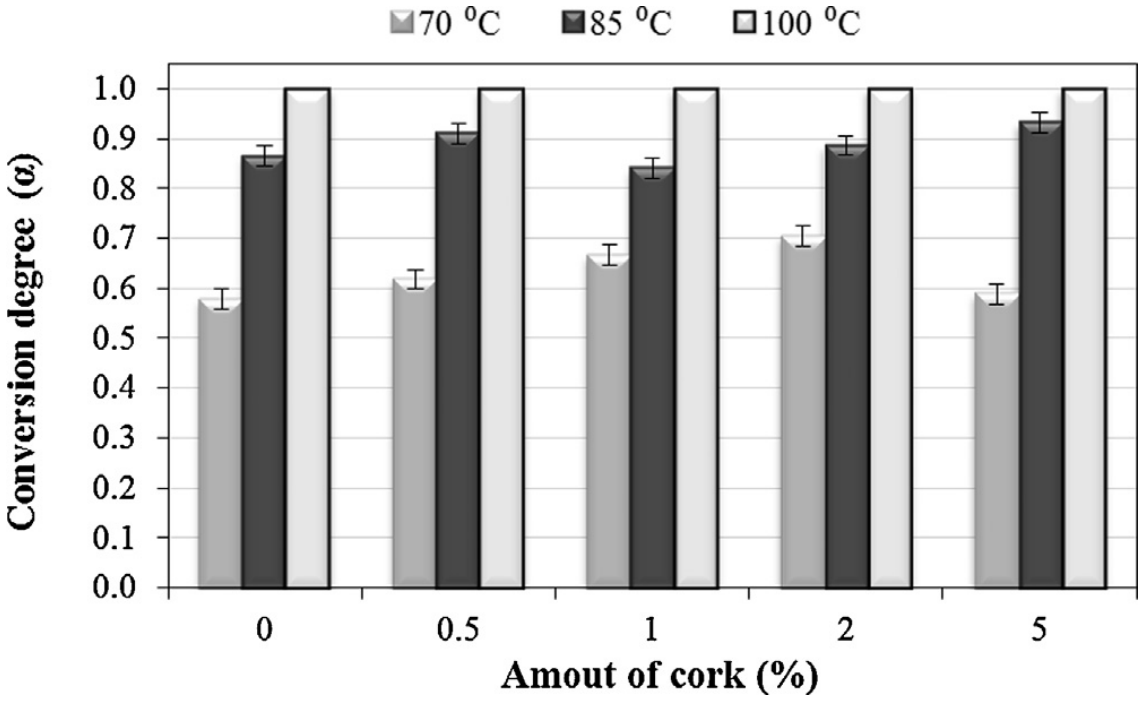

Fig. 2. Conversion degree for neat resin and composites (0.5, 1, 2 and 5% cork) at different temperatures for 30 min.

The determination of the kinetic parameters is a widely used method to study the curing process. The heat evolved at any time during the cure reactions is directly proportional to the extent of conversion [38]. The plot $d\alpha/dt$ versus α allows obtaining the curves

shown in Fig. 3. When these curves are fitted to the Kamal's equation (Eq. (1)) the kinetic parameters are obtained. Kamal's model (according Eq. (1)) agrees well with the experimental curve for conversion values lower than 0.6. For higher conversion degrees, there is no good agreement; this might be due to the fact that the used equation does not take into account diffusion processes. The curing reaction of an epoxy resin with an amine is known to be controlled by the autocatalytic and *n*-order reactions (chemical kinetic) [39]. However, the discrepancy between theoretical and experimental data from a critical conversion value is due to a gradual decrease in the reaction rate and a higher increase of the viscosity. A semi empirical model based on free volume considerations, proposed by Chern and Poehlein, can be used to study the diffusion controlled reaction rate [40].

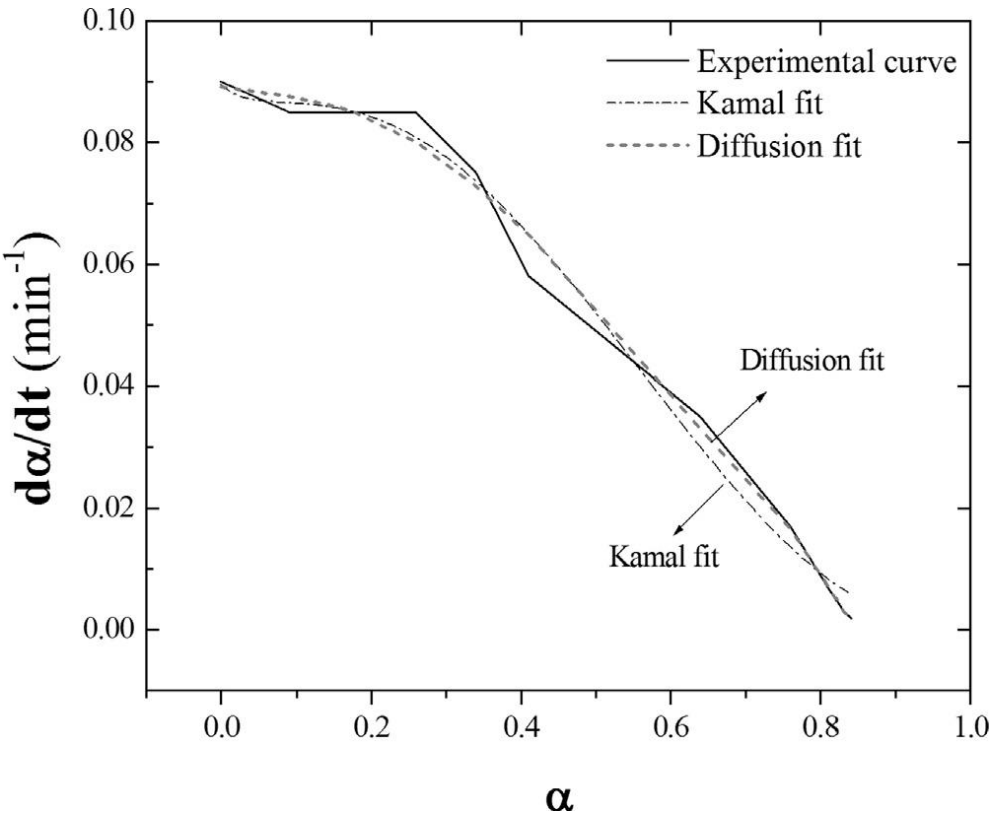

Fig. 3. Eqs. (1) and (6) (Kamal and Kamal + diffusion respectively) fitting curves for the composite with 1% cork measured data at 85 °C.

Using the diffusion factor *F(α),* the reaction rate can be expressed in the following form to account for diffusion effects (Eq. (6)):

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n f(\alpha) \quad (6)$$

F(α) can be computed as $F(\alpha) = 1/(1+e^{C(\alpha-\alpha c)})$, where *C* is the diffusion constant and *αc* the critical conversion degree value. The plot of *dα/dt* versus *α* allows to estimate *C* and *αc*, together with the other kinetic parameters according to Eq. (6). Fig. 3 shows that the diffusion fit has a better correlation with the experimental curve for high conversion degree (<0.6%).

Table 1 shows the kinetic parameters for specimens with different amounts of cork (without cork and 0.5, 1, 2 and 5% of cork particles) at different temperatures (70, 85 and 100 °C), using Eq. (6) (Kamal + diffusion adjustments). In general, the fit is acceptable for all temperatures, with a square of coefficient of correlation R^2 between 0.98 and 1. However, when Kamal's model is applied for the lower temperature, the agreement is poor, around 0.93. This low value is in accordance with the lower value of α, shown in Fig. 1. When the curing of the resin becomes slower, diffusion processes are more important and they are not taken into account in Kamal's equation (Eq. (1)). Analysing Table 1, it can be observed that there is a contribution from the two types of kinetics (autocatalytic and *n*-order according to Eqs. (1) and (6)), although it seems that the autocatalytic reaction is more relevant at the lowest temperature (70 °C) with higher values for k_2. When the temperature is raised, the values of k_1 also increase and therefore the rate of the mechanism of n-order is faster. For specimens cured at 100 °C the n-order is the predominant mechanism, ($k_1 > k_2$). The curing reaction is mainly controlled by diffusion near the completion of the curing [17], so α is just slightly higher than αc. When the reaction is slower, the diffusion processes are more important, since the diffusion processes are time-dependent. The decrease in diffusion controlled reaction rate for higher temperatures is explained by reduction of the molecular mobility due to a higher thermal energy that provides a faster curing. This effect can be observed analysing the kinetic constants k_1,k_2 and k_1/k_2 ratio. In Table 1, it is easily observed that the value of k_2 is higher than k_1 and the k_1/k_2 relation is lower than 1 for

specimens cured at 70 °C. At 85 °C, k_1/k_2 ratio increases to values close to 1, and in some composites it is higher than 1 (0.5 and 5% cork). In general, at 85 °C, autocatalytic and n-order reactions have rates more similar. Also, for specimens cured at 100 °C in some cases k_2 is lower than k_1 and k_1/k_2 ratio is higher than 1.

Table 1 - Kinetic parameters obtained for specimens with different amounts of cork at different temperatures, according Kamal + diffusion model (Eq. (6)).

		α	k_1 (min^{-1})	k_2 (min^{-1})	k_1/k_2	m	n	$m+n$	C	α_c	R^2
70 °C	Araldite	0.58	0.03	0.13	0.21	0.86	2.82	3.68	26.27	0.56	0.98
	+0.5cork	0.62	0.02	0.05	0.37	0.43	1.49	1.92	37.27	0.59	0.98
	+1cork	0.67	0.02	0.11	0.18	0.58	1.96	2.54	33.92	0.65	0.98
	+2cork	0.70	0.02	0.08	0.26	0.45	1.43	1.88	51.50	0.67	0.99
	+5cork	0.59	0.01	0.08	0.12	0.46	1.76	2.22	20.66	0.54	0.98
85 °C	Araldite	0.86	0.08	0.13	0.64	0.87	1.47	2.34	34.27	0.82	0.98
	+0.5cork	0.91	0.11	0.08	1.41	1.89	1.09	2.98	23.79	0.86	1.00
	+1cork	0.84	0.09	0.22	0.41	1.16	1.88	3.04	49.76	0.82	0.99
	+2cork	0.89	0.08	0.13	0.61	0.91	1.35	2.26	36.68	0.86	1.00
	+5cork	0.93	0.10	0.09	1.12	0.50	1.00	1.50	19.86	0.90	1.00
100 °C	Araldite	1.00	0.24	0.14	1.74	0.62	1.03	1.65	2.65	0.72	0.99
	+0.5cork	1.00	0.23	0.10	2.25	0.50	0.84	1.34	3.32	0.74	1.00
	+1cork	1.00	0.21	0.23	0.92	1.08	1.04	2.12	6.67	0.97	1.00
	+2cork	1.00	0.19	0.12	1.57	0.62	0.81	1.43	3.91	0.71	0.99
	+5cork	1.00	0.21	0.11	1.92	0.69	0.90	1.59	3.26	0.80	1.00

Table 1 values support the idea that the cork particles do not exert an influence on the curing process, regardless of the amount. Regarding the order of reaction, it can also be observed that as the temperature increases, the total reaction order gets closer to 1; this is in agreement with other models used by reactions involving reaction n-order with $n = 1$ [27]. However at low temperatures, there are more species (free radicals for autocatalytic reaction) in the reaction and the order reaction is higher. The increase of curing rate with temperature is easily explained by the collision theory. Particles can only react when they collide. If a substance is heated, the particles move faster and so collide more frequently. This will speed up the reaction rate [41]. Also, when temperature is increased, the order reaction is lowered because the reaction is faster and the free radicals disappear quickly. At 100 °C the curing reaction is faster (the collisions between particles increase) and there is no time for diffusion processes; for higher temperatures, the n-order model with an order reaction equals to 1 could be

used in kinetic parameters calculation. However at 85 °C, C increases for neat resin and composite with 1% cork, with a value of k_2 higher than in the other composites (according to Table 1), i.e. the autocatalytic mechanism and the diffusion process remain important. Once the kinetic constant is obtained, the activation energy is calculated using the Arrhenius' equation (Eq. (2)). Two different activation energies were obtained: one corresponding to the epoxy-amine reaction catalysed by the external impurities (norder) and the other one corresponding to the reaction catalysed by the OH groups internally generated (autocatalytic). The calculated activation energy for the two mechanisms (Table 2) shows, as has been mentioned previously, that the *n*-order reaction controls the process of curing the resin and composites. On the one hand, the n-order reaction has a lower reaction rate and on the other hand it needs higher activation energy. It can also be observed that the neat resin in the autocatalytic process does not require energy (the reaction is spontaneous and very fast and it does not change with temperature, as shown in Table 1), while in the composites energy is necessary. In the *n*-order reaction, the energy for the curing process is higher in composites than in the neat resin. Therefore, when cork particles are added, more energy is required for the curing reaction, being this effect more important when adding 5% of particles of cork. This agrees with the steric hindrance caused by the cork particles in the curing process of the resin. Although in general the reaction mechanisms (autocatalytic and n-order) are the same in the composites and neat resin, cork particles influence slightly on the reaction mechanisms. The cork particles could inhibit that the OH groups (formed by opening of the oxirane ring [42]) catalyze the curing reaction, for this reason *Eα* is higher for curing the resin in the composite. Therefore, the cork particles can accelerate or delay the reaction mechanisms. "*A*" is the frequency factor or attempt frequency of the reaction in the Arrhenius equation (Eq. (2)). It indicates the collisions frequency that results in a reaction per time unity. Hence, the factor "*A*" must be much higher in the n-order reaction, as observed

in Table 2. This reaction is caused by collisions between particles. In Table 2 an increment in "A_1" can be seen in n-order reaction when cork particles are added; in autocatalytic reaction, "A_2" is much smaller than "A_1". "A_2" also slightly increases for composites with 0.5% of cork.

Table 2 - Activation energy values calculated from the kinetic constants (Table 1) by Arrhenius's equation (Eq. (2)) and *Ea* obtained as a mean between maximum and minimum of the MFK.

	E_{a_1} (kJ mol^{-1})	E_{a_2} (kJ mol^{-1})	A_1 (min^{-1})	A_2 (min^{-1})	E_a MFK (kJ mol^{-1})
Araldite	75 ± 2	0	7.E + 09	7	80 ± 3
+0.5cork	86 ± 1	21 ± 1	3.E + 11	102	89 ± 1
+1cork	84 ± 1	26 ± 1	1.E + 11	1.24	86 ± 2
+2cork	80 ± 2	17 ± 2	4.E + 10	32	81 ± 1
+5cork	109 ± 3	10 ± 2	5.E + 14	3	103 ± 2

3.1.2. Model free kinetics

The "model free kinetics" (MFK) allows to obtain the activation energy (E_a) as a function of the degree of conversion. The nonisothermal curves at different rates were integrated as a function of time to obtain the conversion degrees. The conversion degree curves show the displacement with the test rate: at higher rates (20°/min) the curing peak appears before and the conversion degree curve is located at higher temperatures and lower times. From these three curves of conversion degree, the software program calculates the activation energy. Fig. 4 shows the activation energy for neat resin and composites. In all materials it is observed that E_a has initial high values, following a gradual reduction to about 90–95% conversion degree and a new increment at the end of the reaction. The initial increase of E_a varies for each composite. The neat resin requires a contribution of energy to start the cure, approximately 91 kJ mol^{-1} (0.1% for curing). Once the reaction has started, E_a needed for the reaction further decreases, and a conversion rate of 3.63% is required (E_a = 59.55 kJ mol^{-1}). E_a decreases to a minimum of 50 kJ mol^{-1} close to a cure of 90%. At that point, E_a begins to rise again to 69 kJ mol^{-1}, when the curing process of the resin is about to finish. Although the curing reaction is exothermic, the reaction requires an initial contribution to occur at the beginning. At the end of the reaction, when the chains are already crosslinked in a high percentage and there are few OH groups available for the reaction progress, a higher value of E_a is also expected. The initial activation energy in the neat resin is 91 kJ mol^{-1}; when cork is added it increases to 128,126,114 and 147 kJ mol^{-1} for 0.5, 1, 2 and 5% cork respectively. E_a at the end of the reaction has a value of 69 kJ mol^{-1} for neat resin, 50 kJ mol^{-1} in the composites with 0.5, 1 and 2% cork, and 59 kJ mol^{-1} for the composite with 5% cork.

When the two methods used for the calculation of the activation energy (Table 2) are compared, similar values are observed between the Ea obtained from Kamal's model and MFK, although the values of MFK are slightly higher in the neat resin and composites, except for composites with 5% cork.

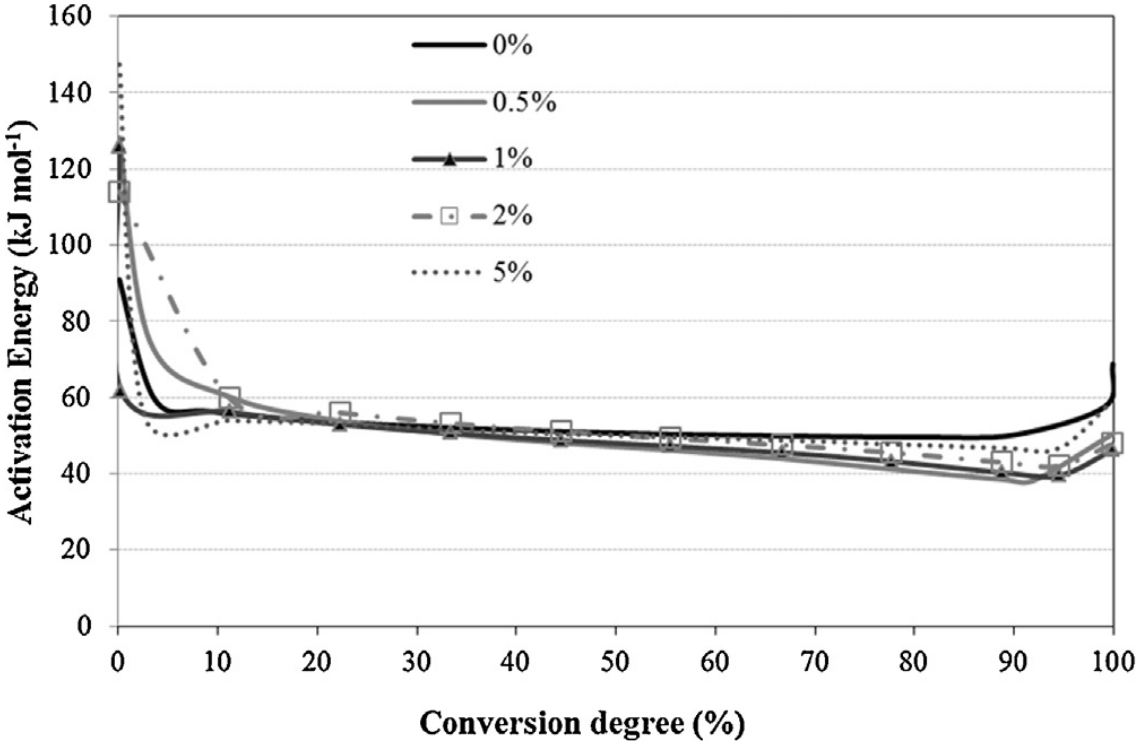

Fig. 4. Variation of activation energy with conversion degree, calculated by model free kinetics, for neat resin (0% cork) and composites.

3.1.3. Applied kinetics

From E_a calculated with MFK the software program allows the kinetics simulation, and the isothermal curves of curing are simulated for different times and temperatures. Table 3 shows the simulated times obtained from MFK model for neat resin at different temperatures and conversion degrees. As expected, the curing time decreases when the temperature increases. At 25 °C the neat resin needs more than 300 min to get a a value of 75%, while at 100 °C in 16 min a 90% of curing is reached. When the simulation at one temperature is compared with the isothermal curve at the same temperature (Fig. 5), a good correlation was obtained, although the simulation is conservative. Table 3 also shows the simulated times obtained from MFK model for neat resin and different

composites at 50 °C and different conversion degrees. Between 40 and 90% conversion degrees, the curing time decreases when cork particles are added. However the cork amount influences the reduction of the curing time, e.g. for 75% of conversion degree when 0.5% of particles are added the curing time decreases from 98 to 67 min and to 89 min for 5% of cork. For a lower conversion degree (from 10 to 30%), the cork particles seem to have a slight influence on the curing initiation. This is in accordance to the high E_a obtained for the composites in the isothermal and non-isothermal tests compared with the low values for the neat resin (Table 2).

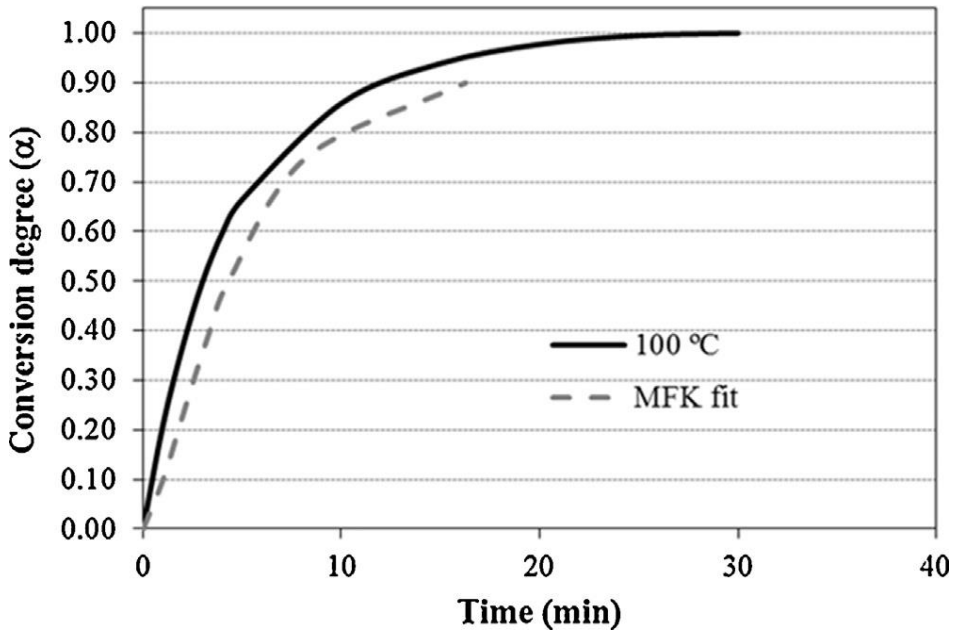

Fig. 5. Conversion degree versus time for neat resin cured exothermically at 100 °C and simulation with MFK at same temperature.

Table 3 - Variation of the curing time (min) with temperature, for 300 min for neat resin and composites by model free simulation.

Conversion degree (%)	Neat resin			Cork amount (%)			
				0.5	1	2	5
	Temperature (°C)			Temperature (°C)			
	25	50	100	50	50	50	50
10	95	17	1	19	16	17	15
20	141	26	2	28	25	26	24
30	180	35	3	35	32	35	33
40	218	44	3.5	41	39	42	41
50	263	54	4	48	47	50	51
75	<300	98	8	67	71	77	89
90	–	199	16	94	100	114	158

3.2. Glass transition temperature

Specimens cured at 50 °C during 10 min and post-cured at 100 °C for 40 min were tested to obtain T_g values. It has been found that these T_g values (measured during the second scanning of DSC) correspond to the maximum degree of cure achieved. Neat resin and composites without hardener were also tested to obtain T_{g0} values. When Eqs. (3) and (4) are applied the plots of the T_g versus the conversion degree are obtained (Fig. 6). Thus, the degree of cure may be provided according to the value of T_g. According to the data sheet of the supplier, this resin has a T_g of 39.5 °C. This represents only an 87% conversion degree. In Table 4, the fit for all materials studied with all necessary parameters to apply Eq. (3) are shown. The analysis of Table 4 values show that the T_{g1} of composites decrease in relation to the neat resin (measurement error ±2). This means that the particles exert a plasticizing effect on the resin. Therefore, differences in mechanical properties must be observed.

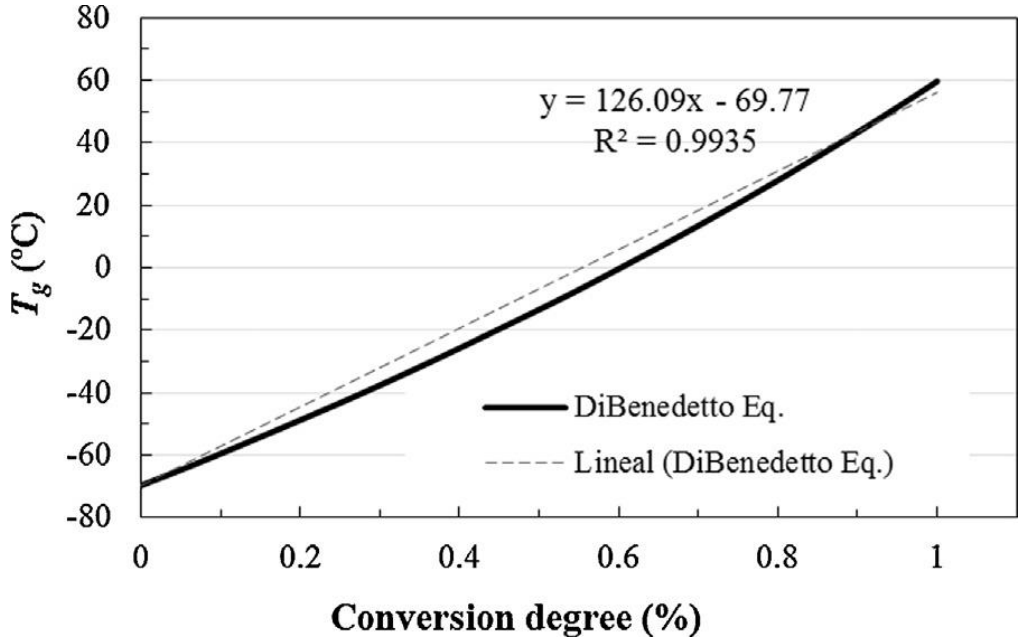

Fig. 6. T_g versus conversion degree for neat resin, according DiBenedetto equation (Eq. (3)) and lineal fit.

Table 4 - Parameters and fit of DiBenedetto equation Eq. (3).

	$T_{g\infty}$ (°C)	$\Delta C_{p\infty}$ ($J\,°C^{-1}\,g^{-1}$)	T_{g0} (°C)	ΔC_{p0} ($J\,°C^{-1}\,g^{-1}$)	λ	Fit equation
Araldite	60	0.44	−70	0.57	0.77	$y = 126.09x - 69.77$
+0.5%cork	55	0.44	−70	0.60	0.74	$y = 121.92x - 70.39$
+1%cork	53	0.43	−66	0.54	0.79	$y = 116.35x - 65.83$
+2%cork	54	0.35	−69	0.50	0.70	$y = 119.30x - 69.49$
+5%cork	55	0.31	−69	0.66	0.47	$y = 113.93x - 69.15$

3.3. FTIR results

To understand better how the micro-particles can influence the curing process of the neat resin, a chemical evaluation was made to Araldite 2020® before cure and after cure. Fig. 7 shows the spectrum in the 4000–450 cm^{-1} wavenumber range for cork, resin (2020A) and hardener (2020B) before curing, and Araldite 2020® and composite with 0.5% cork after, curing. The spectrum before curing (Fig. 7 (2020A) and (2020B)) clearly shows several peaks derived from either the resin or the hardener. Note the oxirane ring at 913 cm^{-1}, considered one of the most characteristic peaks of DGEBA resins. Absorptions at 3364, 3286 and 3178 cm^{-1} are due to the stretching vibration of the

primary amino group of the hardener structure. The amino group presents a peak at 1606 cm^{-1}. There is a very strong peak at 2916 cm^{-1}, due to the stretching vibration of the —CH2— group. The characterization of the spectrum DGEBA molecule can be done by other three absorption peaks: the aromatic carbon oxygen stretching (strong band at 1244 cm^{-1}), the aliphatic carbon-oxygen (1035 cm^{-1}) and the epoxy ether group (916 cm^{-1}). The peaks at 1509 and 831 cm^{-1} can be assigned to p-phenylene groups. After the end of the cure of Araldite 2020®, a decrease in size in the epoxide group and the primary amide peaks (see Fig. 7 (Araldite)) can be observed. In the cured adhesive spectrum, new absorptions appear (3383 cm^{-1}) due to the secondary amine and hydroxyl groups formed during Araldite 2020® cure [7,20,23]. The degree of conversion of an epoxy can be followed by the peaks at 913 (oxirane) and the peak at 1035 cm^{-1} (aliphatic carbon–oxygen). When the adhesive is completely cured, the peak of the oxirane ring is diminished and does not change with time. Cork is a bio-polymer composed of suberin (40%), lignin (22%), polysaccharides (20%) and waxes and other extractives (15%) [43].

Fig. 7 (cork) shows a typical FTIR spectrum of cork. Suberin aliphatic chains can be assigned to the peaks at 2921, 2851 and 1737 cm^{-1}. Asymmetric and symmetric stretching can be observed, respectively at peaks 2921 and 2851 cm^{-1}. The peak 1737 cm^{-1} can be assigned to C=O group. There are other very important peaks such as guaiacyl-type lignin (1509, 858 and 820 cm^{-1}), lignin aromatics C=C (1067 and 1509 cm^{-1}), polysaccharides (1093 and 1034 cm^{-1}), and extractives (1454–1367 cm^{-1}). [43–45].
The epoxy resin modified with cork particles was also analysed by FTIR. Fig. 7 (+0.5cork) shows the FTIR spectra of resins with 0.5% of micro cork particles after curing. Analysing the peaks of the spectra of the epoxy resin without and with different amounts of cork, it is observed that there are no major differences. From the analysis of Fig. 7 (+0.5cork) and compared with Araldite spectrum (Fig. 7), it may be concluded that the there is no formation of by- products after the addition of cork. In this system resin/cork, the cork does not cause any biological or chemical reaction in the resin, neither is there any reaction between them. This is an important result as it proves that the effect of the cork particles on the mechanical properties of the resin is solely due to mechanical interactions between the cork and the resin, as shown in previous studies [5,6].

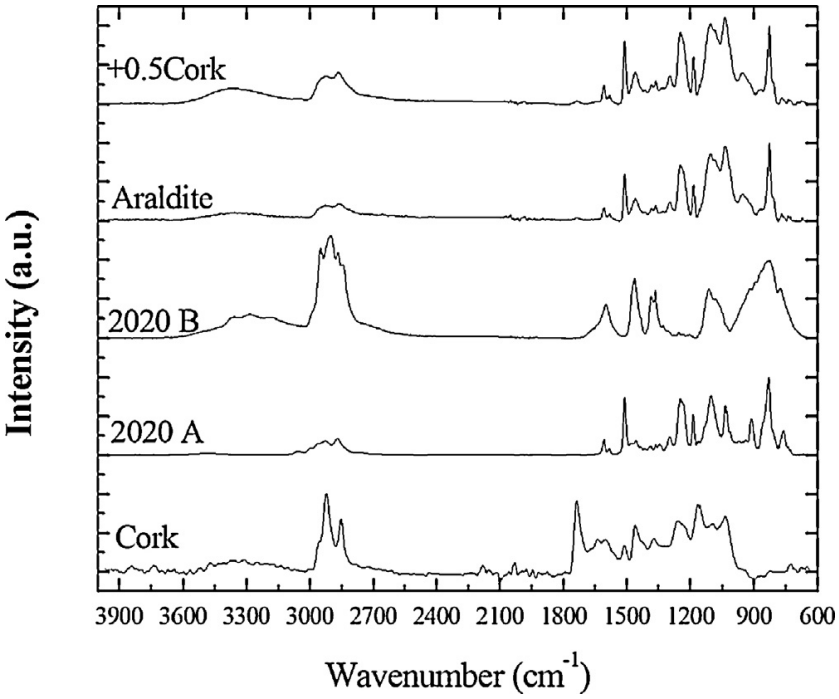

Fig. 7. FTIR spectrum, in the 4000–450 cm^{-1} wavenumber range for: Cork; Epoxy resin (2020 A and B before mixing and after curing (Araldite)) and composite with 0.5% cork after curing (+0.5cork).

3.4. Tensile test results

Neat resin and composites typical tensile stress-strain curves are shown in Fig. 8. The cork particles do not change significantly the tensile strength (50 MPa ±3), although composites show a tensile strength slightly lower. However, the changes in ductility are a little more significant (see Fig. 9), for samples with 0.5 and 1 vol% of cork. Specimens with small amounts of cork (0.5 and 1% of cork) present a higher maximum strain to failure than specimens without cork particles. However, specimens with 2 and 5% cork present a lower value of strain. There seems to be an optimum amount of cork particles for obtaining the best adhesive ductility. Below 1% of cork, the amount is insignificant and above 1% the cork particles start to act as defects since the adhesive becomes more brittle. Fig. 9 also includes the measurements of T_g of specimens with different amounts of cork (0.5, 1, 2 and 5%). Specimens with cork particles present a lower T_g compared with specimens without cork. The T_g values obtained for specimens with cork particles are in line with the tensile test results. It is known that as the T_g decreases, there is an increase in the ductility of the adhesive [1]. Therefore, the composite which has the

lowest T_g (1% of cork) should give the highest ductility, which is consistent with the tensile tests results.

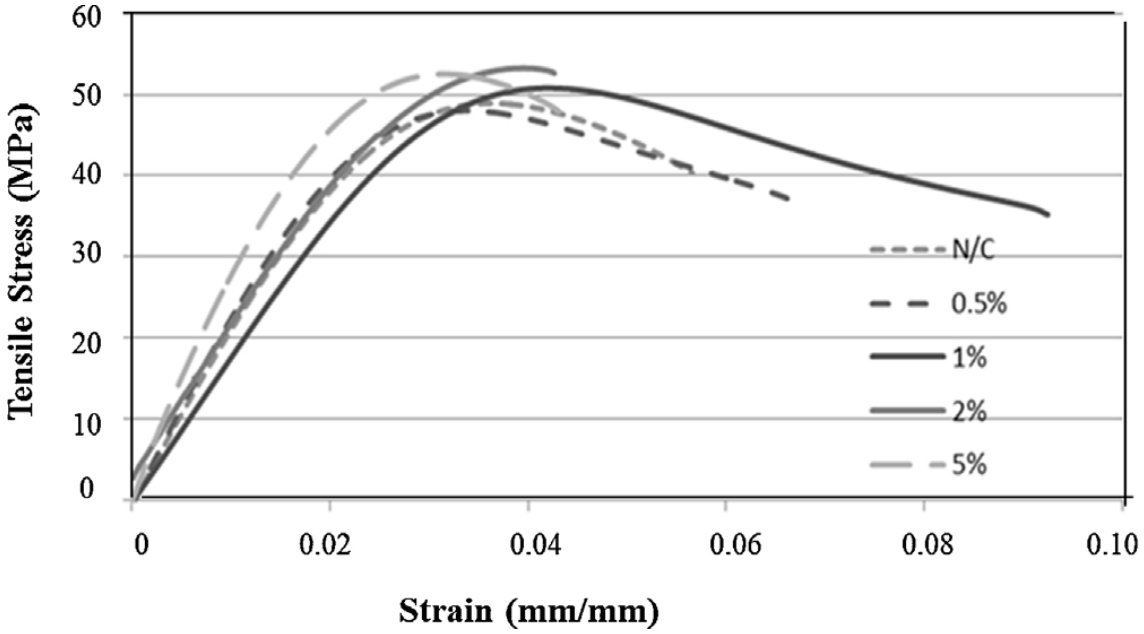

Fig. 8. Tensile stress-strain curve of specimens with different cork amounts (n/cork, 0.5, 1, 2 and 5%).

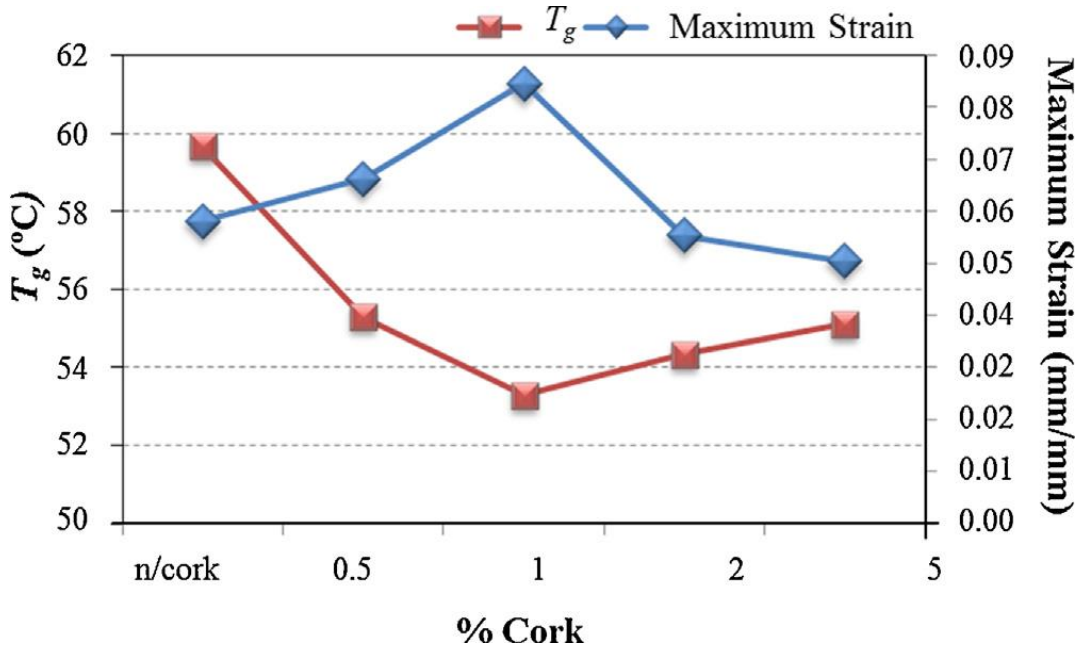

Fig. 9. Comparison between T_g measurements and maximum strain of tensile test specimens with different cork amounts (n/cork, 0.5, 1, 2 and 5%).

4. Conclusions

- The temperature of cure affects the cure of the adhesive: higher temperatures present a higher conversion degree in a short period of time (30 min).
- The diffusion effect is important in the curing process.
- The behaviour during the curing of the composite and neat resin is very similar. At lower temperatures (70 °C) the autocatalytic mechanism is much faster ($k_2 > k_1$) and the diffusion processes are important that n-order mechanism. At the highest temperature (100 °C), the *n*-order mechanism is more important and the curing reaction is fast. However, for all temperatures the mechanism that determines the rate of the reaction is the mechanism of n-order, because it is the mechanism that requires the highest activation energy.
- According to Kamal's model, when cork particles are added, more energy activation is required to carry out curing reaction. However, by MFK simulation, at lower temperatures of 25 and 50 °C, a catalytic effect is observed when the cork particles are added in low percentage. Also, 5% cork particles produce a steric hindrance.
- The FTIR analysis shows that curing of the adhesive leads to the formation of different functional groups of the resin, but the micro particles do not have any chemical reaction with the epoxy resin.
- Analysing all the data from DSC and FTIR, it was concluded that the cork particles have no direct influence on the curing of the adhesive, possibly because the particles introduced stay at the micro level (125–250 μm), and do not affect the molecular structure of the adhesive.
- 1% of cork particles with a structure composed by a limited number of cells with well-preserved cell walls incorporated in the brittle resin give more ductility than other amounts of cork.
- T_g measurements are consistent with tensile tests, showing that specimens with 1% cork have a lower T_g which corresponds to a more ductile behaviour.
- The mechanical properties presented by composite resin/cork are not due to mechanisms inherent to the curing process.

Acknowledgements

Financial support by Foundation for Science and Technology (PTDC/EME-TME/098752/2008 and SFRH/BD/88173/2012) is greatly acknowledged. The authors also want to thank Amorim Cork Composite (Mozelos, Portugal) for supplying the cork powder used.

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Bulk fracture test

Toughness of a brittle epoxy resin reinforced with micro cork particles: effect of size, amount and surface treatment

A.Q. Barbosa[1*], L.F.M. da Silva[2], J. Abenojar[3], M. Figueiredo[2], A. Öchsner[4]

[1]INEGI, Rua Dr. Roberto Frias,400 4200-465, Porto, Portugal

[2] Department of Mechanical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

[3]Materials Performance Group, Materials Science and Engineering Department, Universidad Carlos III de Madrid, Leganés, Spain

[4]Griffith School of Engineering, Griffith University (Gold Coast Campus), Building G39 Room 2.22, Parklands Drive, Southport Queensland 4214, Australia

ABSTRACT

Structural adhesives are increasingly being used for new applications, replacing conventional bonding methods. Epoxy resins are the most common structural adhesives used due to their suitable mechanical, thermal and chemical properties, as well for their low ductility and low toughness. Several researchers, have in the past decades, found it necessary to reverse these properties and find new ways to increase the toughness of these adhesives. There are many processes depicted in the literature on how to increase the toughness of brittle adhesives, the use of rubber particles being one of the most common. The inclusion of particles (nano or micro) is a successful method to improve toughness of structural adhesives. In the present study, natural micro particles of cork are used with the objective of increasing the toughness of a brittle epoxy adhesive. The concept is for the cork particles to act like as a crack stopper leading to more energy absorption. The influence of the cork particle size, amount and the presence of a surface treatment were studied. Cork particles ranging from 38-53 and 125-250 µm were mixed into adhesive Araldite 2020®. The amount of cork in the adhesive varied between 0.25 to 1% in volume. The toughness of the adhesive was assessed through fracture tests, using three-point bending specimens. A Taguchi design experiments was used to understand the influence of each parameter under study (amount, size and presence of surface treatment) and the interaction between them. With this research it was possible

to conclude that cork can improve toughness and cork amount, size and the use of plasma surface treatment have influence on the mechanical properties.

Keywords: Epoxy, Cork, Fracture toughness, Micro-particles

1 – INTRODUCTION

Due to its versatility, adhesive bonding is one of the most used techniques for joining materials. Adhesives can join a wide range of materials (polymers, ceramics, metals) and the combinations of any of those materials [1,2]. Adhesives have been increasingly expanding their applications in the industry and epoxies are the most common structural adhesive used. Structural epoxies adhesives are mainly used due to their good mechanical, thermal and chemical properties [1]. The epoxy microstructure is very useful for applications in structural engineering, because it presents high modulus of elasticity and strength, low creep, and good thermal strength [2, 3]. Nevertheless, the structure of these thermoset polymers also causes brittleness, with a low resistance to the initiation of cracks and their propagation [4, 5]. Consequently, toughening of epoxies has become a necessity to ensure the suitability of these materials for practical applications. Toughening of these adhesives has been widely studied in the past forty years, and nowadays represents a large field of scientific and technological concern. [4, 6-10]. There are some solutions available to improve toughness of brittle adhesives, like the inclusion of particles (inorganic or organic) [11, 12].

Toughness can be defined as the resistance of the material to fracture when stressed, in other words, the ability of a material to absorb energy and plastically deform without breaking. Toughness is one of the main aspects that govern the strength of materials. Hence, it is important to have full awareness of this property in order to develop a reinforced adhesive [13].

The assessment of toughness of an epoxy reinforced with particles can be made by using fracture tests on bulk adhesive specimens and on adhesive-joint specimens. In these fracture tests, a linear elastic fracture mechanics approach is considered [14]. Bulk tests are a good approach to evaluate the adhesive mechanical properties. These specimens are frequently studied as part of the materials development process.

Nevertheless, since there are some requirements that must be assured, the manufacture of bulk specimens is not an easy task. For instance, the presence of air bubbles must be reduced to obtain a complete filling of the mould and uncontrolled exothermic degradation of the adhesive during cure must be avoided. Furthermore, a uniform distribution of the particles must be assured, in case the adhesive has a second phase (for example a reinforcement material).

The properties of the reinforced adhesive are not only based on the properties of adhesive matrix or reinforcing particles, there are other parameters that contribute to the toughness process, which largely influence the outcome of the composite material. The parameters considered in this research are the volume fraction (amount), size of the particle and the interface particle/matrix; considering always a well-dispersed separate phase in the cured adhesive.

The amount of particles dispersed in a structural adhesive matrix is a very important parameter in the subsequent toughening properties of the adhesive [15-18]. The volume of particles is directly related to the nature of the particles and their mechanical properties, so it is crucial have full knowledge of the particles nature and properties. Typically, for ductile particles, the critical strain energy release rate (G_{Ic}) only raises very slowly with the increased volume fraction and then reaches a plateau value[19, 20].

Particle size is an equally noteworthy parameter and should be evaluated attentively. Some studies[21, 22] indicated that, for adhesives with micro particles, fracture toughness increases with particle size, so some concluded that G_{Ic} decreases with an increase in particle size at lower volume fractions, while critical energy releases G_{Ic} drops with increasing particles size. Nevertheless, this statement is not consensual. Additionally, size is a parameter that influences not just the fracture toughness but also the operative toughening mechanisms in modified adhesives [18, 23-25]. Size is a variable that can be controlled, and its importance is perceived at all stages of the production of toughening adhesive and subsequent application.

The interface between the particles and the adhesive is also a key factor in the toughness process. When this parameter is studied, it is expected that the properties of a composite material, considering a specific surface area, are strongly influenced in the case of smaller particles, since its interface constitutes a much larger area within the bulk material. Hence, a good wetting between adhesive and the particles, favouring a

strong bond, should be guaranteed. Consequently, particles will act as crack stoppers and not as defects on the matrix.

Some authors [26] concluded that weakly bonded particles present lower fracture toughness, compared to strongly bonded particles. Furthermore, the bonding strength of the particle/matrix interface is a vital parameter to determine which toughening mechanism is dominant in the filled system, since strengthening the particle/matrix adhesion increases the efficiency of pinning, but suppresses crack tip blunting. This acts as a crack pinning mechanism, where propagating crack is blocked by rigid particles. However, blunting at the crack tip can also originate through localized shear yielding and the formation of a damage zone due to crack diversion, particle fracture, as well as debonding of the particle/matrix interface [27]. Chemistry of the particle surface is also extremely important, as it defines both the rate of wetting and the strength of interaction with the adhesive. Consequently, to ensure appropriate interfacial interactions, their surface properties must be modified accordingly. Frequently it is suggested that some degree of modification or treatment should be applied to all surfaces prior to adhesive bonding, in order to make the surface more receptive to the adhesive. In this study, plasma treatment was used to modify the surface of the cork particles, since, depending on the selected gases, it can substantially increase the surface wettability and decrease the contact angle. There are several proposed models which acknowledge that plasma treatments, crosslink and reticulate the substrate surface, developing a more active surface and improving wettability due to surface oxidation, introducing reactive groups that increase the surface reactivity. Previous studies observed that the plasma treatment increased the wettability of the cork [28, 29].

In this study micro cork particles were used to increase the toughness of a brittle adhesive. Tests were performed to evaluate the influence of the cork by particle size, amount and the presence of a surface treatment. To better understand the influence of each parameter and the interaction between them, the Taguchi method was used.

2- MATERIALS AND METHODS

2.1 – Materials

Araldite 2020®, from Huntsman Advanced Materials (Pamplona, Spain), was the designated adhesive because it is quite brittle, so the improvements on the toughness after the cork particles can easily be perceived. Araldite 2020® is a two component adhesive (100/30 by weight), resin (component A) and hardener (component B). Component A is composed by diglycidyl ether of bisphenol A, (DGEBA) and diglycidyl ether of 1, 4 butanediol (DGEBOH). On the other hand, the component B is composed by isophorone diamine (IPDA).

Cork powder with 38-53 and 125-250 µm size was used. The cork used was supplied by Amorim Cork Composites (Mozelos, Portugal), without any treatment.

2.2 – Surface plasma treatment

Plasma treatment was used to modify the surface of the cork particles since it can considerably increase the surface wettability and decrease the contact angle [30]. Low pressure plasma treatment was performed on a Plasma Cleaner chamber from Harrick Plasma (Ithaca, NY, USA), using air as the gas to produce the plasma on a surface of 70.85 cm^2, at 0.29 atm of pressure. For the treatment in the chamber, 30 W of electric power for 1 minute was used.

2.3 – Manufacture of bulk specimens

The cork was initially mixed with the resin using a centrifuge mixing machine, SpeedMixer DAC 150™ (Hauschild, Hamm, Germany), for 90 seconds at 1500 rpm. Before, the cork was mixed with the resin and after that the hardener was added to the mixture. This procedure was the same for the different amounts and cork size. To ensure a better particle distribution after the mixing, the composite was heated to 50°C for 15 minutes, to increase the adhesive viscosity. Afterwards, the composite was mixed again in the centrifuge mixing machine. This procedure was considered the most simple and effective way to prevent agglomeration of cork particles [31].

After, the mixture was cast in a pre-heated steel mould. Release agent was applied to the mould to ensure an easy release of the bulk specimen. A silicone rubber frame was used to apply a hydrostatic pressure to the adhesive, which was hot pressed (2 MPa) for 15 minutes at 100°C (according to the manufacturer's recommendation cure). Specimens were machined from the plates manufactured with a mould [32]. The specimen production plan, varying cork presence, amount, size of cork particles and the presence of surface treatments, is shown in Figure 1.

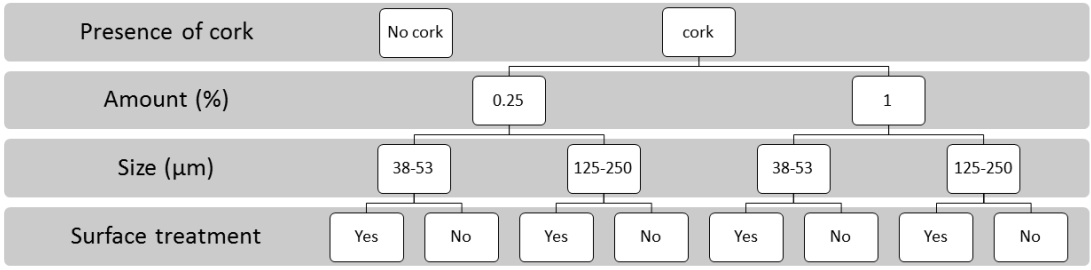

Figure 1 - Schematic diagram of cork specimens with different amounts (% in volume) and size of cork particles and plasma treatment.

2.4 – Tensile tests

Tensile tests were performed to determine the value of Young's modulus for each of the proposed conditions. For tensile tests, dog-bone specimens with 2 mm of thickness were used [33]. The tensile tests were carried out in an Instron 3367 universal testing machine (Norwood, USA), with a capacity of 30 kN. This test was made at room temperature and at a test speed of 1 mm/min. Three specimens were tested for each condition.

2.5 – Fracture tests on bulk specimens- single edge notched bend

Fracture tests could be performed on bulk adhesive and/or adhesive joints. However, when bulk specimens are used, a more accurate determination of the adhesive properties is achieved. The cured plates were machined to single edge notched bend (SENB) specimens, using standard techniques developed for polymers (ISO 2000) [34]. SENB specimens were used to determine the toughness of the epoxy in terms of the critical-stress-intensity factor, K_{Ic}, and the critical strain energy release rate, G_{Ic},

satisfying the requirements of ASTM D5045-99 and ASTM E 399 [35, 36]. SENB geometry consists of a centre-notched beam loaded in three-point bending (see Figure 2). The pre-crack (*a*) was obtained by lightly tapping a razor blade (0.3 mm) into the tip of the machined crack. It is crucial to perform a very sharp pre-crack and eliminate residual stresses around the crack tip, in order to obtain a precise K_{Ic} and G_{Ic} value. The pre-crack length (*a*) ranged from about 5.4 to 6.6 mm. After opening the pre-crack, it was necessary to measure it with the greatest possible accuracy. For this purpose, a magnifying glass (Zeiss/Germany) was used in conjunction with an image capture software, Leica LAS 4.3 (Leica Microsystems/Germany).

The plane-strain fracture toughness tests were carried out in an Instron 3367 universal testing machine (Norwood, USA), with a capacity of 30 kN. This test was performed at room temperature with a crosshead speed of 10 mm/min, which was fast enough to avoid the viscoelastic behaviour of the epoxy [35]. Five specimens were tested for each condition. Figure 2 shows the geometry of SENB specimens used in this study.

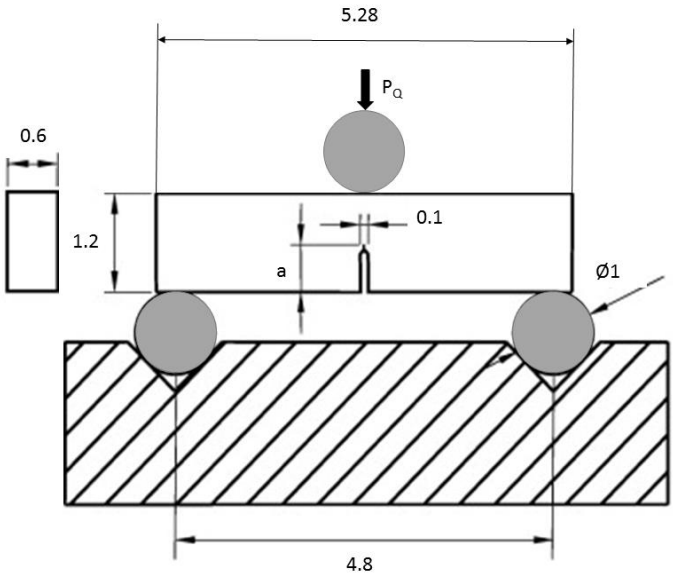

Figure 2 - Single edge notched bend (SENB) geometry specimen used for bulk adhesive fracture testing and test setup (dimensions in mm).

The K_Q values were determined using the following equations [35]:

$$K_Q = \left(\frac{P_Q}{BW^{1/2}}\right) f(x) \qquad \text{(Equation 1)}$$

$$(0 < x < 1)$$

$$f(x) = 6x^{1/2} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{3/2}} \qquad \text{(Equation 2)}$$

Where K_Q is a provisional fracture toughness (MPa.m$^{1/2}$), f the shape factor, P_Q is the maximum load (kN), *B* the specimen thickness (cm), *W* width (cm), *a* the crack length (cm). According to standard ASTM D 5045 it is necessary to check the validity of K_Q via the size criteria. It was calculated $2.5(K_Q/\sigma_y)^2$ where σ_y is the yield stress. If this quantity is less than the specimen thickness, *B*, the crack length, *a*, and the ligament (*W*-*a*), K_Q is equal to K_{IC}. Otherwise the test is not a valid K_{IC} test. The G_{Ic} values were determined using the following equation [35]:

$$G_{Ic} = \frac{(1-v^2)}{E} {K_Q}^2 \qquad \text{(Equation 4)}$$

Where G_{Ic} is the toughness parameter based on energy required to fracture (kJ/m^2) and *v* is the Poisson coefficient.

Standard geometry is recommended over other configurations because these have predominantly bending stress states which allow smaller specimens sizes to achieve plane strain. So, in order for a result to be considered valid, the following criteria must be satisfied:

$$B, a, (W - a) > 2.5\left(K_Q/\sigma_y\right)^2 \text{ (Equation 5)}$$

2.6 – Scanning electron microscopy analysis (SEM)

Scanning electron microscope (SEM) analyses were performed in a JEOL JSM 6301F/ Oxford INCA Energy 350/Gatan Alto 2500 microscope (Tokyo, Japan) at CEMUP (University of Porto, Portugal). This equipment was used to analyse the cork particles, particle distribution and surface fractures. Samples were coated with an Au/Pd thin film, by sputtering, using the SPI Module Sputter Coater equipment, for 120 sec and with a 15mA current.

2.7 – Particle size analysis

Particles size analysis was accomplished using a Malvern Mastersizer 2000 (Malvern, United Kingdom). This equipment was used to evaluate the cork particle size distribution. This technique was used to complement the results obtained in SEM. Three tests were made for each condition.

2.8 – Taguchi design experiments

The Taguchi method was the methodology used to design the experiments [37]. For the selection and definition of a Taguchi experimental plan, seven crucial steps must be considered:

- Identification of system factors and response;
- Selection of the levels of the factors to experiment;
- Selection of the appropriate Taguchi orthogonal array;
- Assignment of factors and/or interactions to the columns of the orthogonal array;
- Conducting the tests;
- Data analysis: average response graphs, ANOVA (analysis of variance)
- Performing confirmation tests [38, 39]

The Taguchi orthogonal array used contains three variables, corresponding to the size, amount and surface plasma treatment, therefore, a $L_8(2^7)$ it was applied (Table 1). The $L_8(2^7)$ allows to quantify the main effects and interactions between the variables

considered. The influence of each variable and its interactions was assessed by the average response and the analysis of variance, ANOVA (SuperANOVA version v1.11, Abacus Concepts, Inc. 1991).

Table 3 - Taguchi $L_8(2^7)$ orthogonal array, with all variables studied (size, amount and plasma surface treatment).

Test	**Variable**		
	Size µm	**Amount %**	**Plasma surface treatment**
1	53-38	0.25	with
2	53-38	0.25	without
3	53-38	1	with
4	53-38	1	without
5	125-250	0.25	with
6	125-250	0.25	without
7	125-250	1	with
8	125-250	1	without

3 -RESULTS AND DISCUSSION

3.1 - Cork particles characterization

The cork particles size, shape and wall thickness were analysed in SEM, for particles with and without plasma surface treatment. In both cases, particles with 125-250 µm size presented a honeycomb structure composed by several cells, some open (edges of particles), but also closed cells (particle core) (see Figures 3 and 4). Particles with 38-53 µm size have damaged cell walls, and in some cases these particles present only cell walls fragments (see Figures 5 and 6). When analysing the surfaces that have been treated with plasma, some differences are observed compared to the particles that were not treated. The thickness of the cell walls of the treated particles is smaller than that of the particles that did not have surface treatment. Measurements were performed at

various cell walls and a decrease of cell wall thickness of 3.6% was observed in particles sized between 38-53 µm and a decrease of 3.3% in particles sized between 125-250 µm. These results suggest that the plasma treatment is responsible for the erosion of the cell walls.

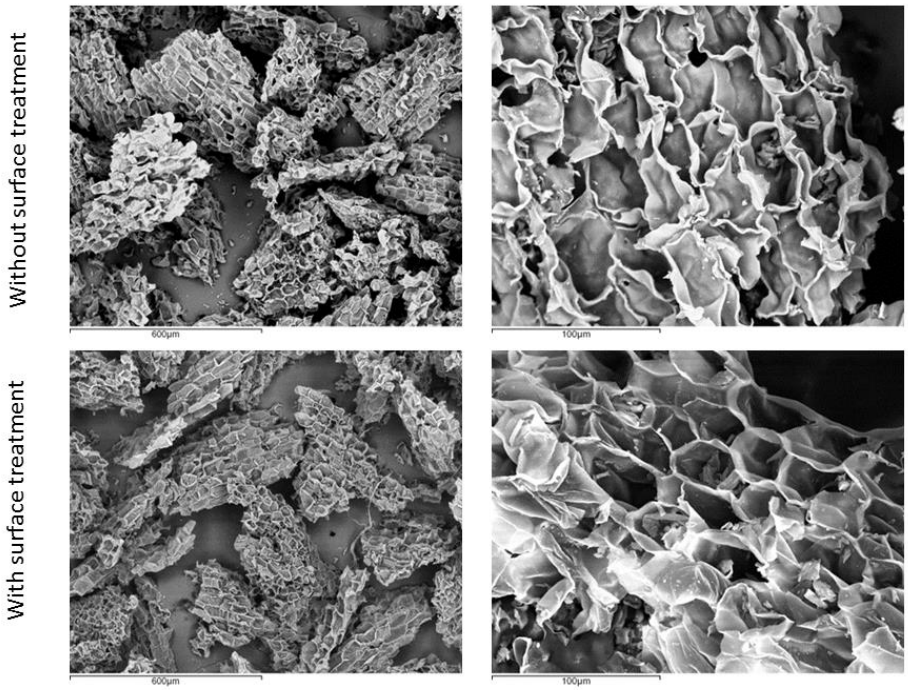

Figure 3 - Cork particles characterization with and without surface treatment, 125-250 µm size.

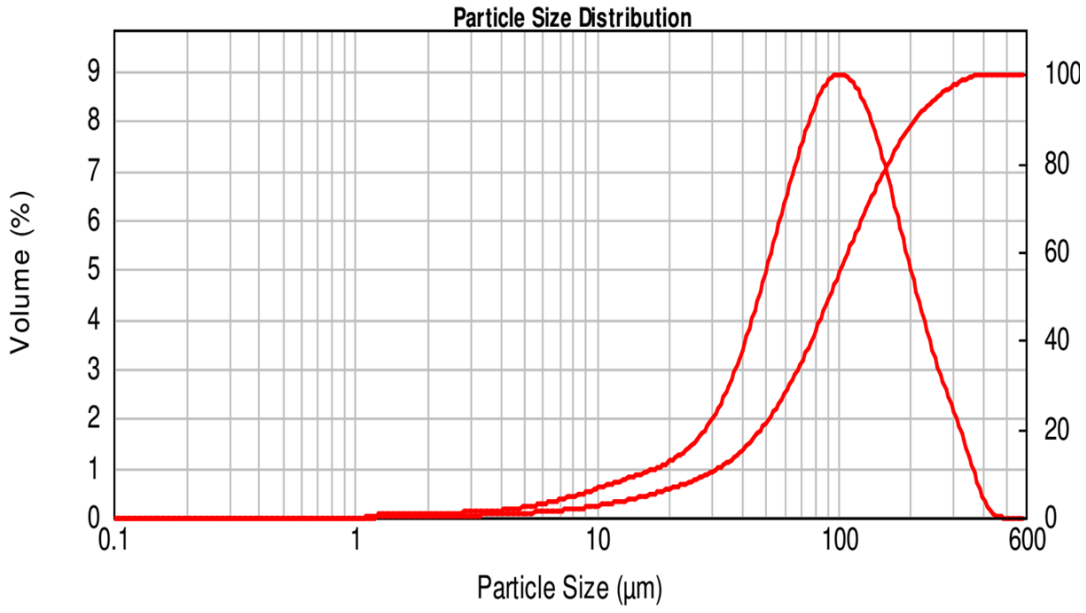

Figure 4 - Particle size distribution of cork particles with 125-250 µm size.

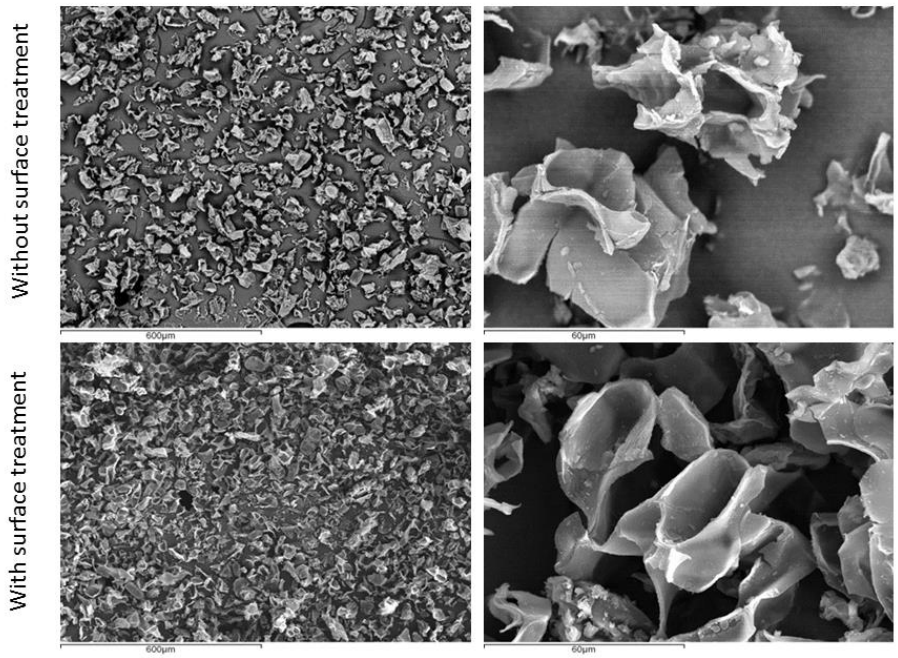

Figure 5 - Cork particles characterization with and without surface treatment, 38-53 µm size.

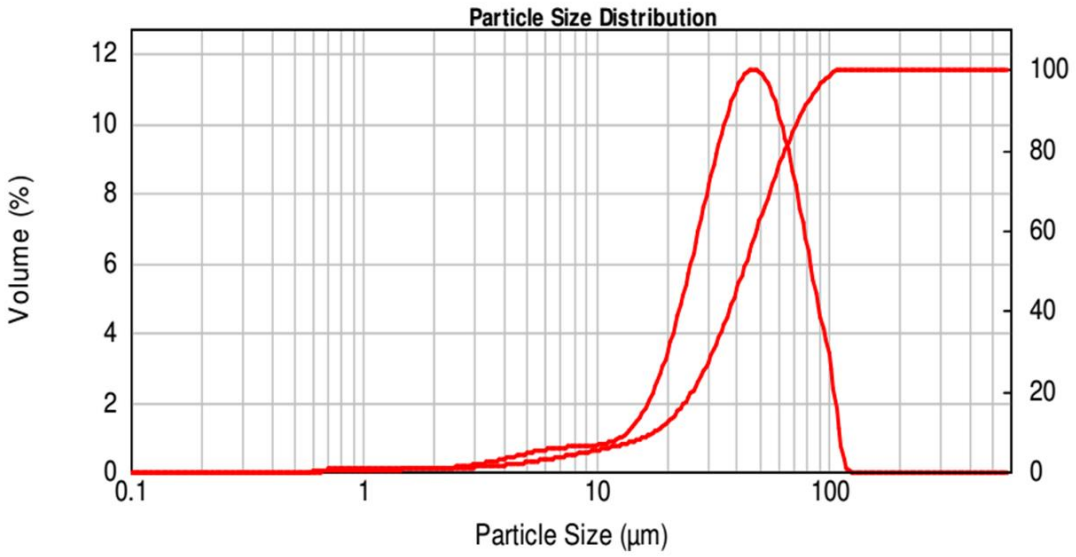

Figure 6 - Particle size distribution of cork particles with 38-53 µm size.

3.2 – Tensile tests

In previous studies it was observed that the presence of cork particles (different size and amount) changes the mechanical properties of the adhesive [31]. In order to evaluate the Young's modulus, tensile tests were performed. Analysing Figure 7 it can be clearly observed that the Young's modulus varies with the size, amount and surface treatment of cork particles and is an important parameter to evaluate the toughness of an adhesive, used to calculate the value of G_{Ic}.

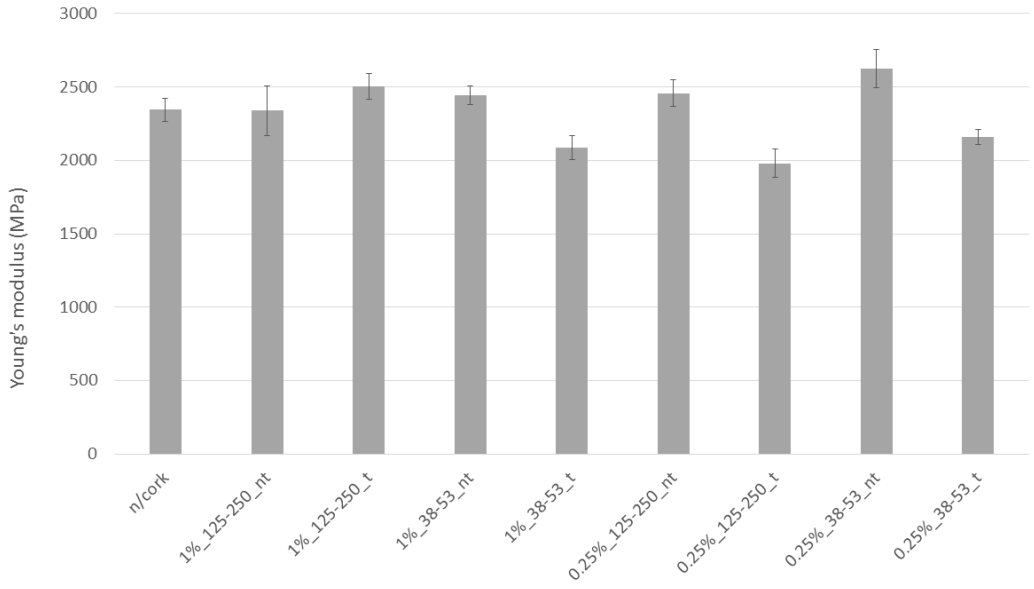

Figure 7 - Young's modulus of specimens with different amount, size and surface treatment of cork particles. t- with surface plasma treatment; nt – without surface plasma treatment

3.3 –Fracture tests on bulk specimens

Three-point bending tests were conducted to evaluate the mode I critical strain energy release rate (G_{Ic}) of the neat resin and epoxy reinforced with micro particle of cork. Analysing the data represented in Figure 8, it is observed that the amount, size and surface treatment influence the adhesive toughness. Specimens with cork which have surface treatments feature G_{Ic} values lower than those presented by the neat resin. And also, for the same amount of cork, specimens with surface plasma treatment present lower G_{Ic} values. On the other hand, the samples with cork which were not subjected to surface treatment show higher values of G_{Ic} compared to that of the neat resin.

Specimens with 1% of cork present the highest increase compared to the neat resin: 191% and 241% for specimens with 125-250 and 38-53 µm, respectively. Specimens with 0.25% do not show a significant increase as compared with 1% amount, compared to neat resin the increase is more moderate: 103% and 129% for specimens of 125-250 and 38-53 µm, respectively.

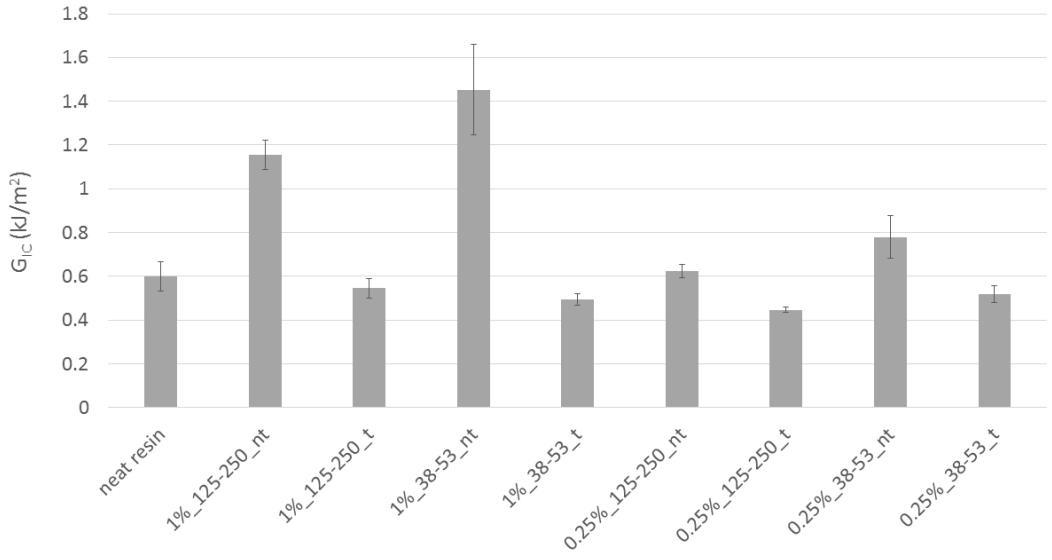

Figure 8 - Fracture toughness of SENB specimens of epoxy reinforced with micro cork particles (different amount, size and surface treatment) and neat resin. t- with surface plasma treatment; nt – without surface plasma treatment.

3.4 –Fracture surface analysis

In order to have a complete grasp of the effect of the particle amount, size and surface treatment on fracture mechanisms, fractographic studies of the SENB specimens fracture surface were carried out, using SEM. This analysis of the fracture surface can be very useful in order to understand the mechanical phenomena occurring during fracture. As previously discussed, the amount, size and surface treatment are responsible for different mechanical properties. Figure 9 and Figure 10 show fracture surfaces with different cork amounts and size for specimens without and with plasma surface treatment, respectively. In both figures, it is evident that micro cork particles are well spread and randomly distributed in the epoxy matrix, and that the fracture surface

shows a brittle behaviour. In Figure 10 the fractures surfaces present a quite smooth fracture surface in the slow growth zone. Outside this area, there are spaced “rib” markings perpendicular to the direction of crack growth, in the crack speeding zones, being more evident in specimens with 1% amount 38-53 µm size. It is possible to observe that the major influence on the fracture surface derives from the particle amount. Specimens with 1% of cork present a less brittle surface, comparing to specimens with 0.25% of cork. Regarding the particles size, it is possible to conclude that specimens with smaller particles, present a less brittle behaviour than specimens with bigger particles. These results are in agreement with the results presented in Figure 9.

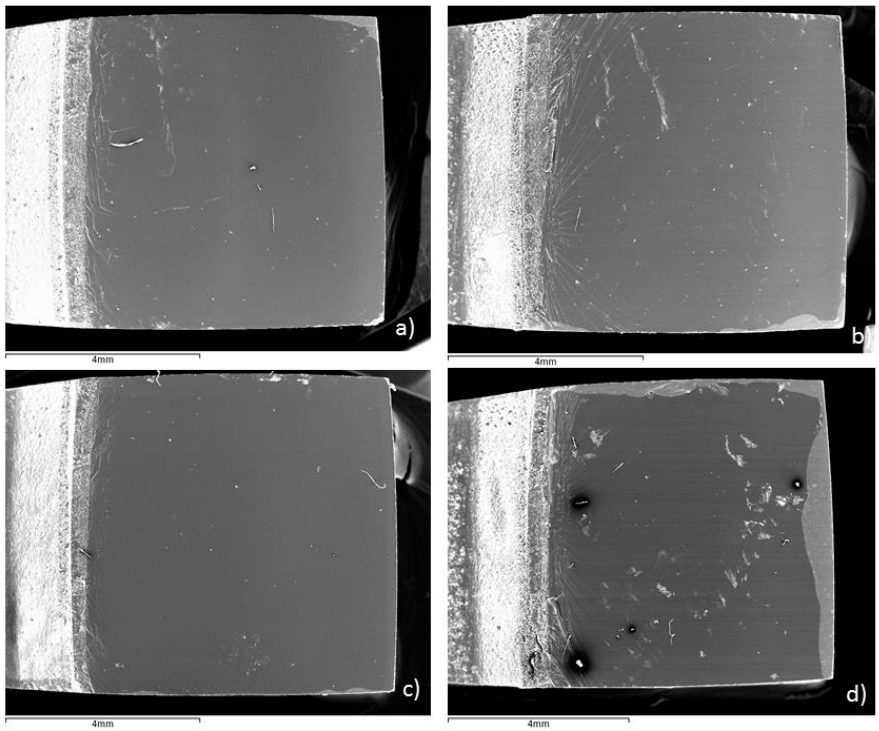

Figure 9 - Fracture surface for specimens without plasma surface treatment; a) 0.25% amount 38-53 µm size; b) 1% amount 38-53 µm size; c) 0.25% amount 125-250 µm size; d) 1% amount 125-250 µm size.

Figure 10 shows that specimens with plasma surface treatment have a more brittle fracture surface than specimens without plasma surface treatment. All the fractures display one slow crack at the of the crack growth and one fast crack growth zone when the instability criterion for crack growth is met with the increasing load.

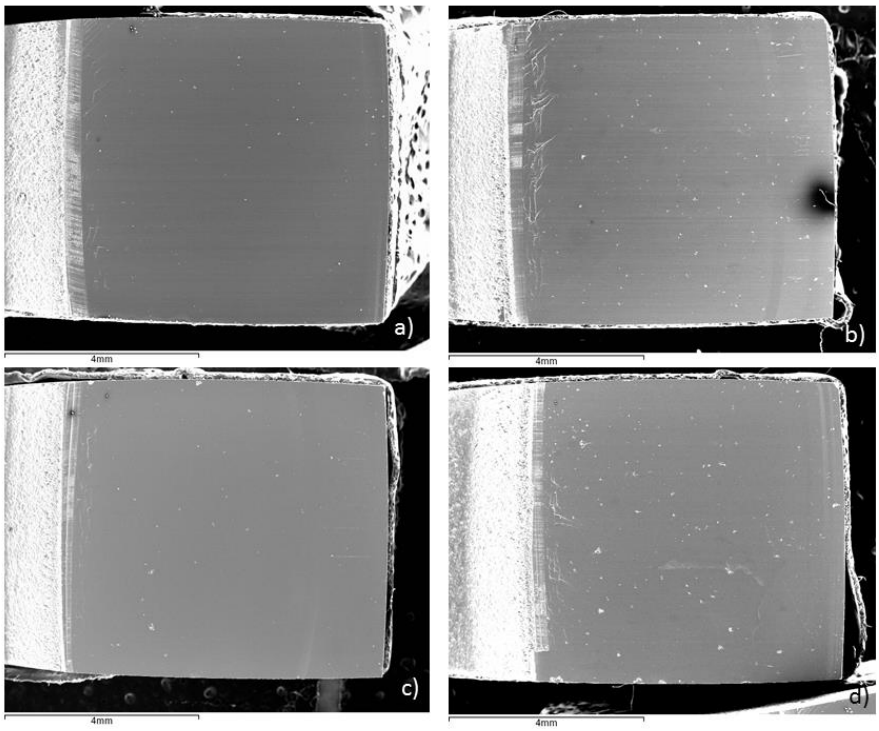

Figure 10 - Fracture surface for specimens with plasma surface treatment; a) 0.25% amount 38-53 µm size; b) 1% amount 38-53 µm size; c) 0.25% amount 125-250 µm size; d) 1% amount 125-250 µm size.

3.5 –Analysis of G_{IC} results - analysis of variance and average response

Despite the findings presented in the previous section, it is still difficult to trace a pattern behaviour between the size and amount of incorporated cork and plasma surface treatment. Thus, using a Taguchi orthogonal array (Table 1) is a great tool to analyse trends and observe which variable has the greatest influence and interactions between the given possibilities. In this table p-value is the value for $\alpha < 0.05$ of significance and P is the contribution. Table 2 presents the ANOVA of the data with 95% confidence, and it is easily observed that surface treatment demonstrates the major influence on the fracture toughness results (45.1% of contribution), followed by the amount (16.9%); size is the parameter with less influence (1.1%), is not significant for 95% of confidence. Analysing Table 2, it is also possible to observe the interaction between the chosen parameters, coming to the conclusion that the strongest interaction is amount vs surface treatment, with 12.7% of contribution.

Table 4 - ANOVA analysis with all parameter and interactions, considering G_{Ic}.

Source	*df*	*Sum of squares*	*Mean square*	*F-value*	*P-value*	*P (%)*
Amount (%)	1	0.86752	0.86752	28.38559	0.001	16.9
Size (µm)	1	0.08429	0.08429	2.75810	0.1062	1.1
Surface treatment	1	2.26170	2.26170	74.00320	0.0001	45.1
Amount (%) vs size (µm)	1	0.00451	0.00451	0.14753	0.7034	-0.5
Amount (%) vs surface treatment	1	0.65709	0.65709	21.50007	0.0001	12.7
Size (µm) vs surface treatment	1	0.06757	0.06757	2.21097	0.1465	0.7
Residual	33	1.00855	0.03056			24.1
total	39	4.951230				100

According to the analysis, surface treatment presents the highest influence on the fracture toughness results (45%). Figure 11 represents the main effect of surface treatment. Specimens with plasma surface treatment present a lower value of G_{Ic}, on the other hand, specimens without surface treatment present higher G_{Ic} values but also a higher dispersion of the results. As this study is aimed to achieve the best combination to improve the toughness of the adhesive, it can be concluded that the surface treatment will not be the best option. While the surface treatment improves the properties of wettability between the adhesive and cork particles, the cork particles mechanical properties and structural integrity are compromised.

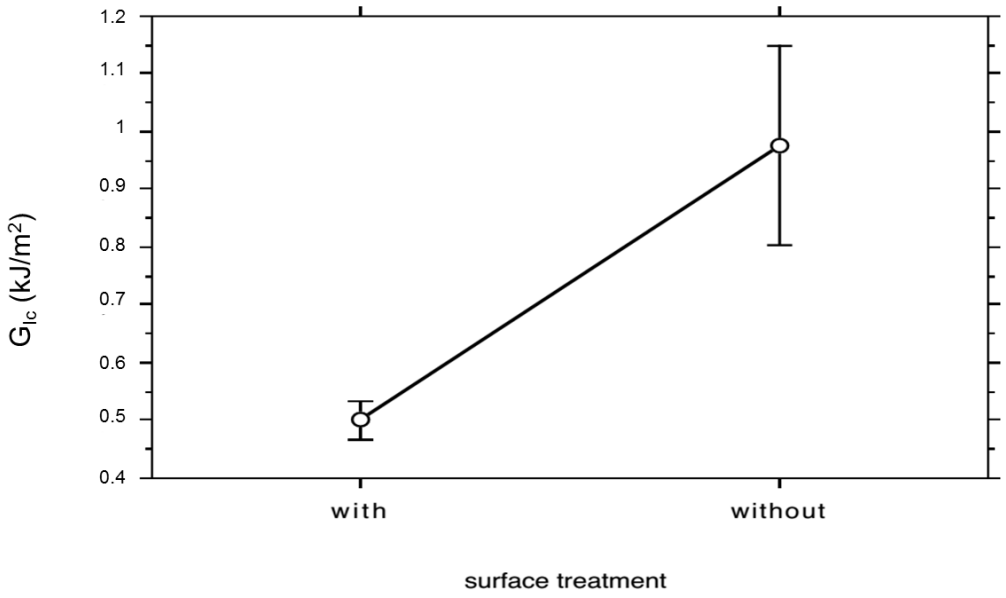

Figure 11 – Main effect of cork particles surface treatment on fracture toughness, average results with 95% confidence error bars.

Figure 12 represents the effect of particle amount on fracture toughness. It is observed that specimens with 1% of cork show higher values of G_{Ic}, although presenting larger dispersion. Cork particles do not have a standardized geometry; its structure may vary depending on biological and mechanical factors, which are extremely difficult to control. So there is an inherent dispersion of results that stems from the conditions of the cork particles. With the increase of the amount of cork particles, the results dispersion also increases, as seen in Figure 12. As mentioned in Table 3, the cork particles amount represents an influence of 16.9% on G_{Ic} results. This result can also be observed by the line slope which joins the two graphed values. The lower the influence of a parameter, the lower the slope of the line.

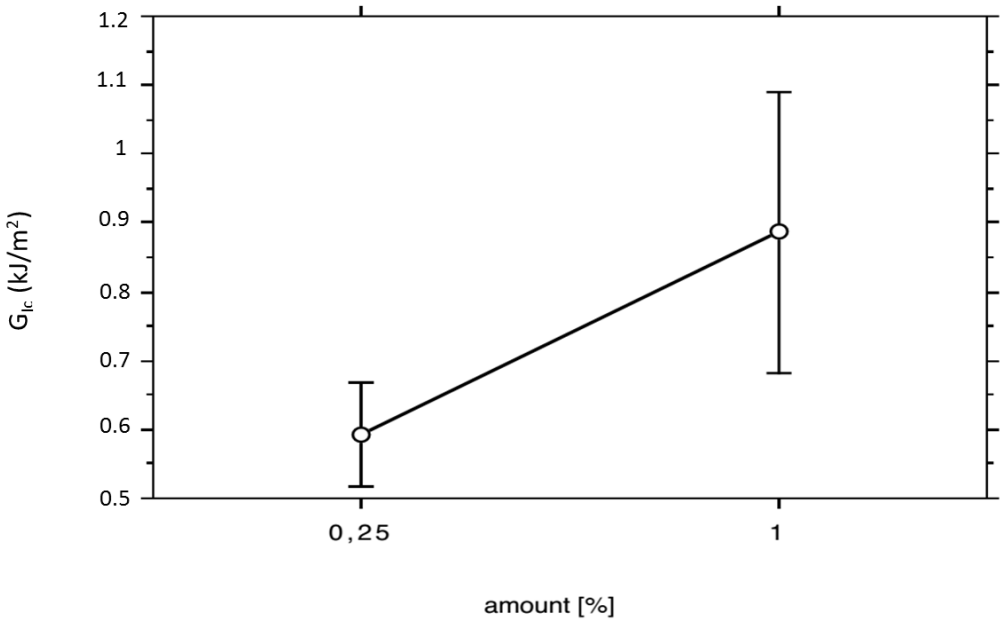

Figure 12 – Main effect of cork particles amount on fracture toughness, average results with 95% confidence error bars.

Figure 13 shows the effect of size on fracture toughness. The fracture toughness of specimens reinforced with small particles, presents higher values compared to specimens reinforced with larger particles. Although, the scatter in both cases is significant, it is equally difficult to draw meaningful conclusions regarding this parameter. For 95% of confidence is not significant, as already verify with ANOVA.

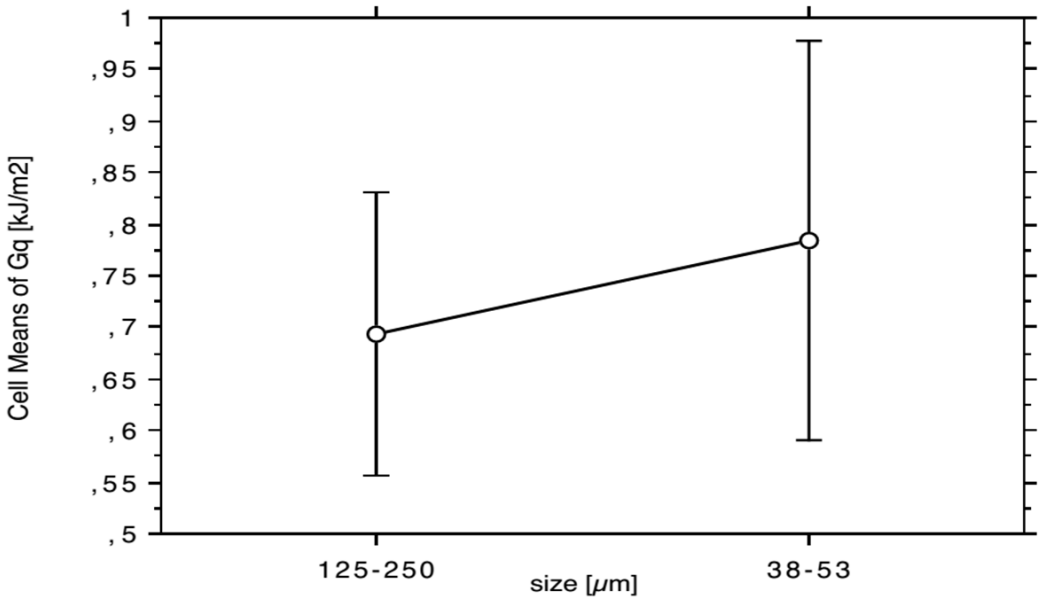

Figure 13 – Main effect of cork particles size on fracture toughness, average results with 95% confidence error bars.

Figure 14-16 present the interactions between the three parameters: amount, size and surface treatment. It is important to study the influence of each parameter, but also the interaction between parameters to better optimize the process in order to select the best combination possible. Figure 14 presents the interaction between particle amount and surface treatment. This interaction represents a contribution of 12.7% on total variation, indicating a high interaction. With plasma surface treatment, there are no significant fluctuations with varying particle amounts, but without plasma treatment it is clear that specimens with 1% of cork particles show a higher G_{Ic}, comparing to 0.25% of cork.

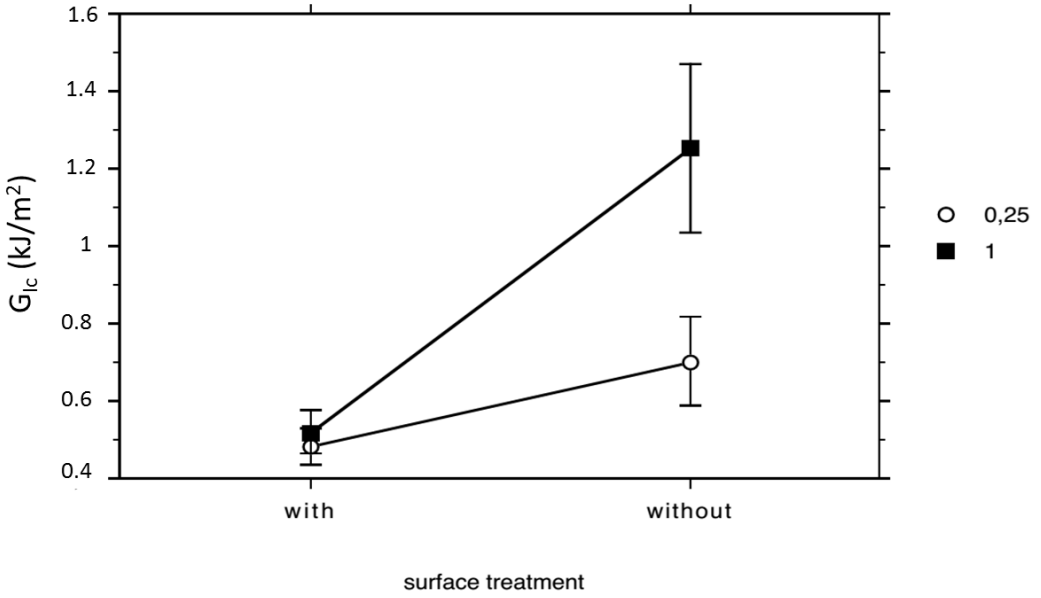

Figure 14 – Interaction on effect of cork particles amount vs surface treatment on fracture toughness, average results with 95% confidence error bars.

Figure 15 presents the interaction between surface treatment and particle size, which represents a contribution of 0.7 %. Similarly, when comparing the interaction between surface treatment and particle amount versus the interaction between surface treatment and particle size, surface treatment is shown to exert an important influence. Specimens with plasma surface treatment present low toughness values, regardless of particle size. Inversely, the behaviour of specimens without plasma surface treatment differs with particle size, as specimens with small particles present higher values of G_{Ic}. However, it must be noted that there is significant dispersion in these results and therefore this can only be considered as a trend.

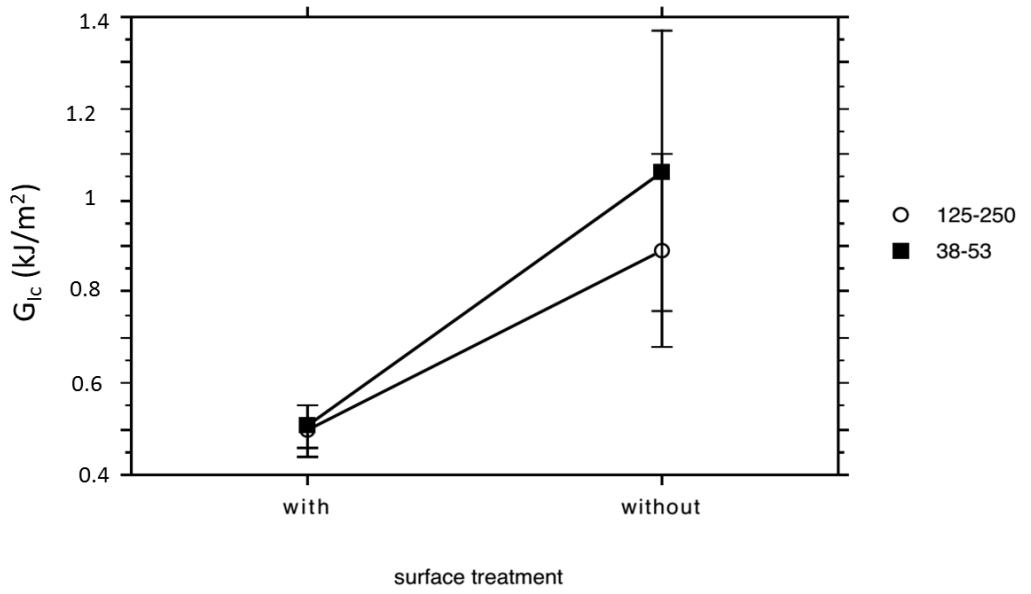

Figure 15 – Interaction on effect of cork particles size vs surface treatment on fracture toughness, average results with 95% confidence error bars.

Figure 16 shows the interaction between size and amount of cork particles, which represents the lowest contribution (-0.5%). In a first analysis, small particle amounts show lower values than higher amounts, regardless of size. However, the dispersion in both cases is significant, not being possible to draw firm conclusions concerning this interaction.

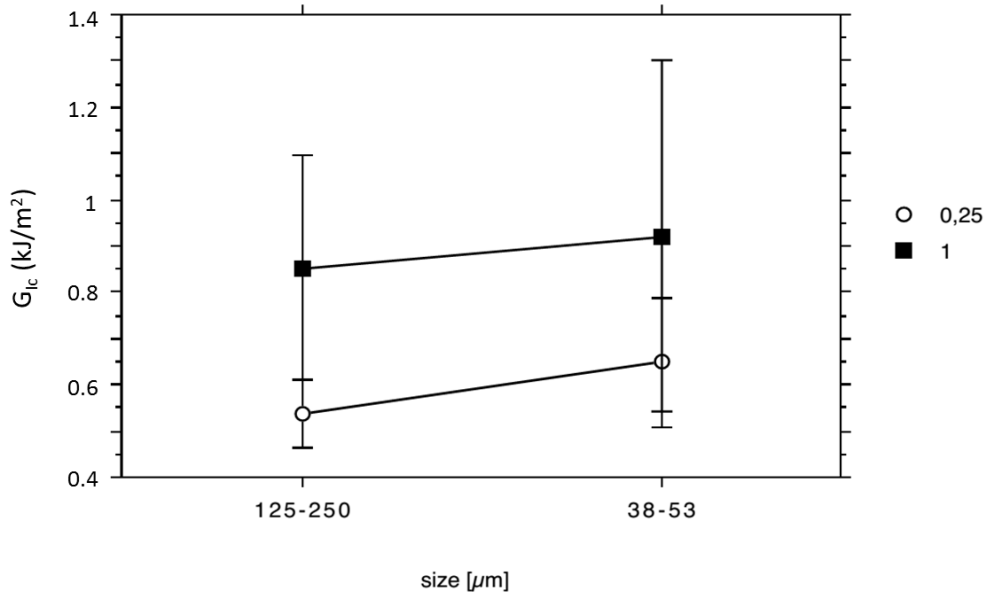

Figure 16 – Interaction on effect of cork particles amount vs size on fracture toughness, average results with 95% confidence error bars.

3.6 –Taguchi analysis of G_{Ic} results - multiple regression

A multiple regression can be used to obtain a G_{Ic} prediction, constructed using the relationship between the three independent variables. The regression coefficients of G_{Ic} values versus the three independent variables are given in Table 3.

Table 5 - Regression coefficients of G_{Ic} values versus 3 Independents, with R^2 of 0.65

	Coefficient	*Std. error*	*Std. Coefficient*	*t-Value*	*P-value*
Intercept	0.80674	0.09495	0.80674	8.49690	<0.0001
Amount (%)	0.39272	0.09264	0.41859	4.23938	0.0001
Size (μm)	-0.00065	0.00049	-0.13048	-1.32147	0.1947
Surface treatment	-0.47557	0.06948	-0.67587	-6.84508	<0.0001

With these data points it is possible to formulate an equation that allows to predict the mechanical behaviour of the adhesive by altering the size, amount and the application of surface treatment of micro cork particles (see Equation 6). In this equation, surface treatment is a dummy variable, taking the value “0” for specimens without plasma surface treatment and “1” for specimens with plasma surface treatment. This equation

is valid for particle size between 38-250 µm and amount between 0.25 and 1%, with a determination coefficient (R^2) of 0.65.

$$G_{Ic} = 0.80674 + 0.39272 \times Amount - 0.00065 \times size - 0.47557 \times surface\ treatment$$

(Equation 6)

The experimental results were used to validate the formulated equation. In addition to the previous tested conditions, three additional conditions that have not been used for the formulation of the equation were tested: neat resin, specimens with 5% 125-250 size without surface treatment and specimens with 1.5% 125-250 size without surface treatment. The values presented by the specimen neat resin and 1.5% 125-250 size without surface treatment are not covered by Equation 6, being outside of its range of values. However, this analysis was made to observe if the values of the equation can be extrapolated. Figure 17 presents the experimental values and also the analytical values obtained by Equation 6. Analysing the data, it was found that the correlation between the experimental values and the analytical values is not always perfect. However, the equation proves to be a useful tool to predict the mechanical behaviour of the composite material, as it provides a reasonable estimate of the experimental value. Moreover, as observed for the results of the samples of 1.5% and 125-250 particle size without surface treatment, it is not advisable to extrapolate the results to values outside the range of variables considered, since the prediction may not be precise.

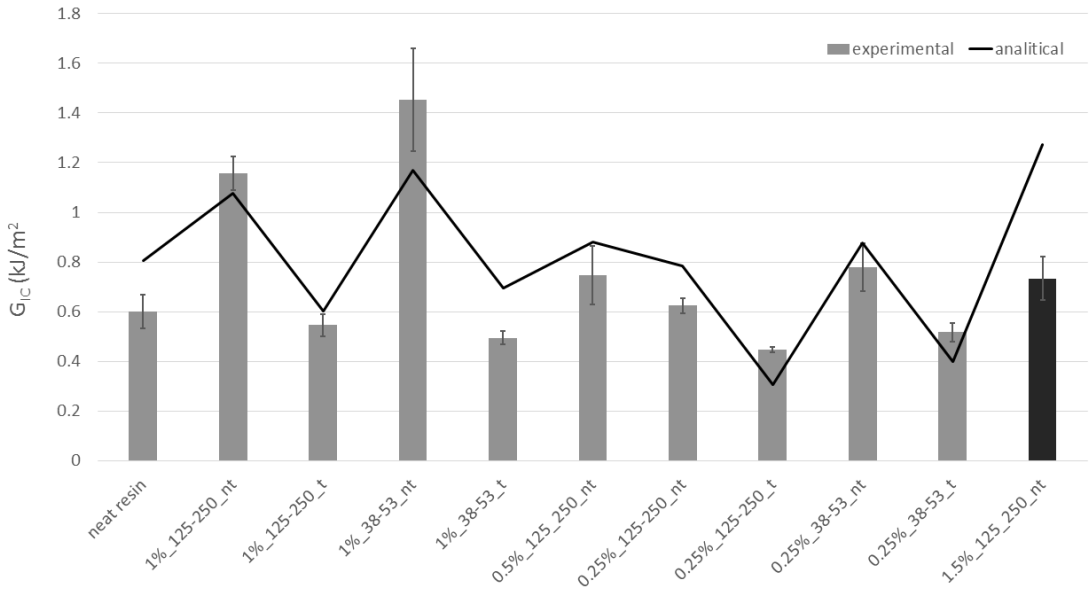

Figure 17 – Comparison between the experimental value and the analytical values of G_{Ic}.

4 – CONCLUSIONS

The effect of particle size, amount and surface plasma treatment of micro cork particles on the fracture toughness of a brittle epoxy resin was evaluated through tensile tests and bulk fracture tests, and later analysed using the Taguchi method. These tests were performed on neat epoxy resin and epoxy resin reinforced with cork particles. The following conclusions can be drawn:

Plasma treatment is responsible for an erosion of cell walls, leading to a decrease in cell wall thickness;

Young's modulus varies with the size, amount and plasma surface treatment of cork particles and is an important parameter to evaluate the toughness of an adhesive used to calculate the value of G_{Ic};

The particle amount, size and plasma surface treatment have an influence on the adhesive toughness. Specimens reinforced with cork particles which were subjected to surface treatments feature G_{Ic} values lower than those of the neat resin. In contrast, the specimens with cork without surface treatment show higher values of G_{Ic} compared to those of the neat resin;

Fracture surfaces are in agreement with the G_{Ic} values: higher values of G_{Ic} are consistent with less brittle fracture surfaces;

The Taguchi method is a practical tool to analyse parameters and observe variable influences and their interactions. Surface treatment shows the main influence on the G_{IC} results, followed by the particle amount; particle size is the parameter with less influence. Regarding the interaction between the parameters, the strongest interaction is amount vs surface treatment;

The formulated equation is shown to be an expedited tool for predicting G_{IC} results.

ACKNOWLEDGEMENTS

Financial support by Foundation for Science and Technology (PTDC/EME-TME/098752/2008 and SFRH / BD / 88173 / 2012) are greatly acknowledged. The authors especially thanks the collaboration of Eng. Claudia Lopes and the Department of Metallurgical and Materials Engineering of Porto University.

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Paper 6

Hygrothermal degradation

Hygrothermal aging of an adhesive reinforced with micro particles of cork

A.Q. Barbosa[1]*, L.F.M. da Silva[2], A. Öchsner[3]

[1]INEGI, Rua Dr. Roberto Frias, 400, 4200-465, Porto, Portugal

[2] Department of Mechanical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal

[3]Griffith School of Engineering, Griffith University (Gold Coast Campus), Building G39 Room 2.22, Parklands Drive, Southport Queensland 4214, Australia

ABSTRACT

In the present study, natural micro particles of cork are used with the objective to increase the toughness of a brittle epoxy adhesive. The cork particles act as a crack stopper, leading to more energy absorption. This fact occurs because cork presents a remarkable combination of properties (low density, low cost and sustainability of the raw material). Adhesives are susceptible to the presence of moisture in the environment. There are several studies that refer that moisture can degrade the molecular structure of the adhesive, and therefore, its mechanical properties. The main objective of this research is to investigate the effect of moisture on the degradation of an adhesive reinforced with micro cork particles, knowing that cork presents a great capability to absorb water. The water absorption and desorption characteristics have been studied, for specimens without cork and with 1% cork, 125-250 μm. The moisture uptake behaviour in the adhesive was studied to obtain the coefficient of moisture diffusion. The effect of water exposure on the mechanical properties and glass transition temperature was also investigated. It was observed that the presence of water alters the mechanical properties of the adhesive (with and without cork), but these changes are not permanent.

Keywords: Adhesive, Cork, Moisture, Hygrothermal aging, Mechanical properties

1 – INTRODUCTION

Adhesive joints show several advantages compared to other solutions to join materials [1,2]. Nevertheless, all adhesives present the capability to absorb water molecules, as well as other low-molecular-weight substances, when they are in the presence of moisture (water-containing atmosphere or immersed in water), even at ambient temperature [3,4]. Hence, understanding the bonding character of water molecules in epoxy is crucial to understand hygrothermal effects [5].

The degradation of adhesively bonded joints through the effects of moisture is one of the biggest problems and prevents a wider implementation of adhesives in structural applications [3,6]. The amount of water absorbed is directly proportional to the degradation increase of the polymeric matrix [7]. Epoxy resins are widely used as matrix for structural adhesives due to their good mechanical properties [8,9]. Nevertheless, these properties are strongly affected by water absorption, which causes plasticization [10], decrease of the glass transition temperature (T_g) and reduction of their mechanical strength [9,11,12]. According to several authors [11,13] water can be present in epoxies in two distinct forms:

1. Free water that fills the micro cavities of the network;
2. Water bond by strong interactions with polar segments (glycidyl epoxy rings or the nitrogen atoms of the amine compound).

Some effects of moisture uptake are reversible, such as plasticisation and swelling. Others are irreversible processes (micro-cracking and hydrolysis), promoting the degradation of adhesive properties, not only mechanical but also thermal and physic-chemical [14,15].

Materials reinforced with natural fibres or particles are increasingly being used in the adhesives industry because they are light, cheap and renewable; they are used in a large range of applications, from sporting goods to automotive and aerospace industry [16]. Thus, it is increasingly urgent to study how these new composite materials behave when they are in an environment with high moisture content. The major concern for the use of natural materials is their susceptibility to moisture absorption and the effect on physic-chemical, mechanical and thermal properties [17,18]. In general, the degradation

of these composite materials is severely affected by the presence and nature of particles, since the degradation occurs preferentially in the resin-particle interface. Hence, it is imperative to understand the behaviour of these adhesives under adverse conditions, in order to predict their long-term performance [19].

Many authors have studied the effect of moisture on reinforced composite materials (fibres), observing that the interface between matrix and reinforcement separates in the presence of moisture, thus reducing the efficiency of the stress transferred between the two components. This effect leads to reduced material mechanical, physical and thermal properties. Some authors concluded that in reinforced materials, the degree of degradation is directly proportional to moisture uptake [7].

In this study, different temperatures of deionized water were used to observe how the diffusion occurs in a brittle epoxy resin reinforced with micro cork particles and observe how the mechanical and physic-chemical properties change with the moisture uptake, below its T_g. Dog-bone specimens were loaded in tension to observe the influence of moisture in the mechanical properties. The effect of moisture on the T_g was measured using a dynamic mechanical analysis type apparatus. A Fourier transform Infrared spectroscopy (FTIR) apparatus was used to evaluate the influence of moisture in the chemical chains in the epoxy resin with and without cork particles.

2 – Experimental

2.1 – Materials

Cork powder with 125-250 µm size was used. The authors have shown in a previous study that this size corresponds to the best mechanical properties of the composite resin/cork [2,20]. The cork used was supplied by Amorim Cork Composites (Mozelos, Portugal), without any treatment.

The selected adhesive was Araldite 2020®, from Huntsman Advanced Materials (Pamplona, Spain). Araldite 2020® is a two component adhesive (100/30 by weight), epoxy resin (component A) and hardener (component B). Component A is composed by diglycidyl ether of bisphenol A, (DGEBA) and diglycidyl ether of 1, 4 butanediol

(DGEBOH). On the other hand, the component B is composed by isophorone diamine (IPDA).

This adhesive is a transparent epoxy with low viscosity (150 mPa.s), that cures at 100°C, within 15 minutes. The Young's modulus of this adhesive is typically 3100 MPa. This material was selected because it is rather brittle, so the improvements on the tensile strength after the cork particles inclusion can easily be observed.

2.2 – Manufacture of bulk specimens

A preliminary study was made on the most appropriate way to mix epoxy resin with cork, because particle aggregation is also expected when mixing cork particles in an epoxy resin [20]. The cork was initially mixed with the epoxy resin using a centrifuge mixing machine, SpeedMixer DAC 150™ (Hauschild, Hamm, Germany), for 90 seconds at 1500 rpm. Then, cork was mixed with the resin and after that the hardener was added to the mixture. Even for specimens without cork, the mixture resin + hardener, was made according to this procedure.

However, a sufficiently uniform distribution of the cork particles was not reached, due to the low density of the cork particles and the adhesive low viscosity. To have a better particle distribution after the mixing, the composite was heated to 50°C during 10 minutes, to increase the adhesive viscosity. After that, the composite was mixed again in the centrifuge mixing machine. This procedure permitted to obtain a uniform particles distribution.

After mixing the cork particles with the resin and hardener, the mixture was cast in a pre-heated steel mould. Release agent was applied to the mould to ensure easy release of the bulk specimen. A silicone rubber frame was used to apply a hydrostatic pressure to the adhesive, which was hot pressed (2 MPa) for 15 minutes at 100°C (according to the manufacturer's recommendation cure schedule). Specimens were machined from the plates manufactured with the mould [21].

2.3 – Bulk adhesive absorption and desorption

For moisture diffusion studies, the bulk adhesive was machined to rectangular plates with dimensions 60 mm x 60 mm and a thickness of 1.0 ± 0.1 mm, to assure that diffusion is one dimensional [22]. Three specimens were prepared for these studies, one for each condition (no cork and 1% cork). The surfaces of the specimens were lightly abraded using sand paper to remove any silicon film or release agent from the bulk surface.

Before immersion, specimens should be dried to constant mass at a temperature that ensures thermal stability of the material. The specimens were conditioned in an oven at a temperature of 50 ± 2°C and 10% of moisture to remove the absorbed moisture from the surrounding environment during the specimen's preparation.

The weight of the specimen was measured using a microbalance with 1 mg accuracy (Kern-Toledo, Balingen, Germany), since typically in epoxies water absorption is higher than 1%. After the specimen weight was constant, specimens were then immersed in deionized water at a temperature of 50 ± 2°C and at room temperature (RT). The temperature of 50 °C was selected according to ISO 62:2008 [23], approximately 20 °C below the T_g to ensure that only physical processes are taking place and there are no changes in the chemical nature of the polymer [1]. Room temperature was chosen because it is the temperature at which the adhesive will usually work. Three specimens of each condition were immersed in a water bath, which ensured that the entire surface is exposed to the liquid medium. The specimens were immersed until the mass of moisture absorption stabilized, called infinite mass (M_∞). After M_∞ was reached, the same specimens used in the absorption test were used to calculate the diffusion rate of moisture in the desorption stage. The desorption test was carried out at 50 °C to accelerate the process, as at RT the test duration is much higher.

2.3.1 – Gravimetric method and swelling measurement

The weight was measured periodically till saturation was achieved. Before weighing, the specimens were removed from the water bath and the surface was wiped off using a dry cloth. The weighing process was carried out as fast as possible to avoid the drying process having a significant effect on the absorbed moisture. This procedure was always

performed with the use of gloves to avoid surface contamination of the specimens. The moisture uptake *Mt* was calculated using equation 1:

$$M_t = \frac{(W_t - W_0)}{W_0} \times 100\% \qquad \text{(eq. 1)}$$

Where w_t is the mass of the specimen at any point in time during the immersion testing and w_0 is the initial constant mass. The saturation mass uptake is defined as being when the weight gain from three successive measurements differs less than 1% of the overall weight gain.

The same procedure that was used for the rectangular plate was employed to measure the moisture absorption of the bulk dog-bone, T_g and FTIR specimens.

Swelling was also periodically measured with a micrometer (Mitutoyo, Mizonokuchi Japan), as a relative dimensional increase as follows:

$$\Delta V/_{V_0} = \frac{V_f - V_0}{V_0} \qquad \text{(eq. 2)}$$

where V_f is the volume of the adhesive after aging and V_0 is the volume of the adhesive plate beforehand [2].

2.3.2 – Diffusion analysis

The absorption/desorption behaviour of the neat epoxy resin and epoxy resin /cork can be quantified by the diffusion coefficient (*D*). The ability of water molecules (or any penetrant molecule) to move among the epoxy resin is quantified by the diffusion coefficient. Fick's law applied to single free-phase diffusion is the most common approach for modelling moisture sorption. Using Fick's Law can easily predict the mass of water absorbed or desorbed. In case of moisture uptake, the mass of water absorbed increases linearly with the square root of time, then, gradually slows until reaching an equilibrium plateau (M_∞). In the case of desorption, the process is the same but the mass of water decreases linearly. Generally, the moisture absorption/desorption of adhesives under hygrothermal conditions can be described by Fick's law (considered a one-dimensional diffusion through an infinite plate of thickness, named *h*) [25,26]:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \quad \text{(eq. 3)}$$

Where *D* represents the coefficient of diffusion, *c* is the concentration of water and *t* is time. Crank [3] suggests a simplification of this equation, showing that for the initial stage of the process where M_t/M_∞<6, the resulting relationship can be applied:

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}h}\sqrt{Dt} \quad \text{(eq. 4)}$$

Where:

$$M_t = M_\infty - M_\infty \frac{8}{\pi^2}\sum_{n=1}^{20}\frac{1}{(2n-1)^2} exp\left[-\frac{(2n-1)^2 D\pi^2}{h^2}t\right] \text{(eq.5)}$$

Rearranging equations 3 and 4, the relationship for *D* is given by:

$$D = \pi\left(\frac{h}{4M_\infty}\right)^2\left(\frac{M_t}{\sqrt{t}}\right)^2 \text{(eq. 6)}$$

2.4 – Tensile tests

For tensile tests, dogbone specimens with 2 mm of thickness were used. The tensile tests were carried out in an Instron 3367 universal testing machine (Norwood, USA), with a capacity of 30 kN. This test was made at RT and at a test speed of 1 mm/min. Three specimens were tested for each condition.

2.5 – Measurements of the glass transition temperature (T_g)

Glass transition temperature measurements were carried out by use of a dynamic mechanical type analysis method initially developed by Adams and co-workers [28]. The method involves excitation of the test specimen during the heating and the cooling. T_g is measured by registering the damping of the specimen as a function of temperature. T_g is defined as the temperature at which the peak value of damping is observed. This method of analysis is quite fast (19°C/min) so that it does not dry the specimen during heating [20,28].

The method used to attach the specimen consists in using a pre-cured sheet of adhesive which is attached between an aluminium beam and a constraining steel sheet by a bolt. For glass transition temperature measurements, the bulk adhesive was machined to rectangular plates with dimensions 30 mm x 12 mm and a thickness of 2.0 ± 0.1 mm.

2.6 – Scanning electron microscopy analysis (SEM)

Scanning electron microscope (SEM) analyses were produced in a JEOL JSM 6301F/ Oxford INCA Energy 350/Gatan Alto 2500 microscope (Tokyo, Japan) at CEMUP (University of Porto, Portugal). This equipment was used to analyse cork particles, particle distribution and surface fractures. Samples were coated with a Au/Pd thin film, by sputtering, using the SPI Module Sputter Coater equipment, for 120 sec and with a 15mA current.

2.7 – Fourier transform infrared spectroscopy (FTIR)

Evaluation of FTIR spectra can be a great help to understand the effects of hygrothermal aging, since if irreversible damage occurs, the intensity of absorption bands for relevant groups will decrease or increase [29]. FTIR measurements were carried out by use of a PerkinElmer Spectrum Two apparatus (Waltham, USA). Wave lengths of (4000 – 600) cm^{-1} and 0.2 cm^{-1} of scanning velocity were used. These tests were carried out with a $LiTaO_3$ detector (15700-370 cm^{-1}) and a KBr window. Two tests were performed for each condition. The Spectrum 10 PerkinElmer software Spectrum (Waltham, USA) was used for the data analyses. Bulk specimens with 1 mm thickness were used.

3 -RESULTS AND DISCUSSION

3.1 - Absorption

3.1.1 - Moisture diffusion of the bulk adhesive

Figure 4 shows the average moisture uptake for bulk adhesive Araldite 2020® and Araldite 2020® with 1% of cork versus the square root of time over the thickness ($\sqrt{t}/l$) in deionized water at 50°C, for absorption and desorption stages and at RT for absorption. Unlike the tests performed at 50°C, at RT only absorption tests were performed, since at this temperature the tests are quite slow. A Fickian fit was made to the experimental points and it was observed that the experimental and analytical curves have a good agreement. It is observed that for absorption and desorption at 50°C, the samples of the neat epoxy resin and those of the epoxy resin with cork particles have a quite similar behaviour (see also Table 1).

Analysing the results of absorption (Table 1 and Figure 1), it is observed that the temperature has a great influence in this process. The value of diffusion of specimens at 50°C is higher than the values obtained at RT which means the water molecules penetrate more quickly into the interior of the polymer chains. It can be also observed that there is no great variation between specimens with and without cork. This shows that the cork does not prevent water movement or is a promoter of increased water absorption.

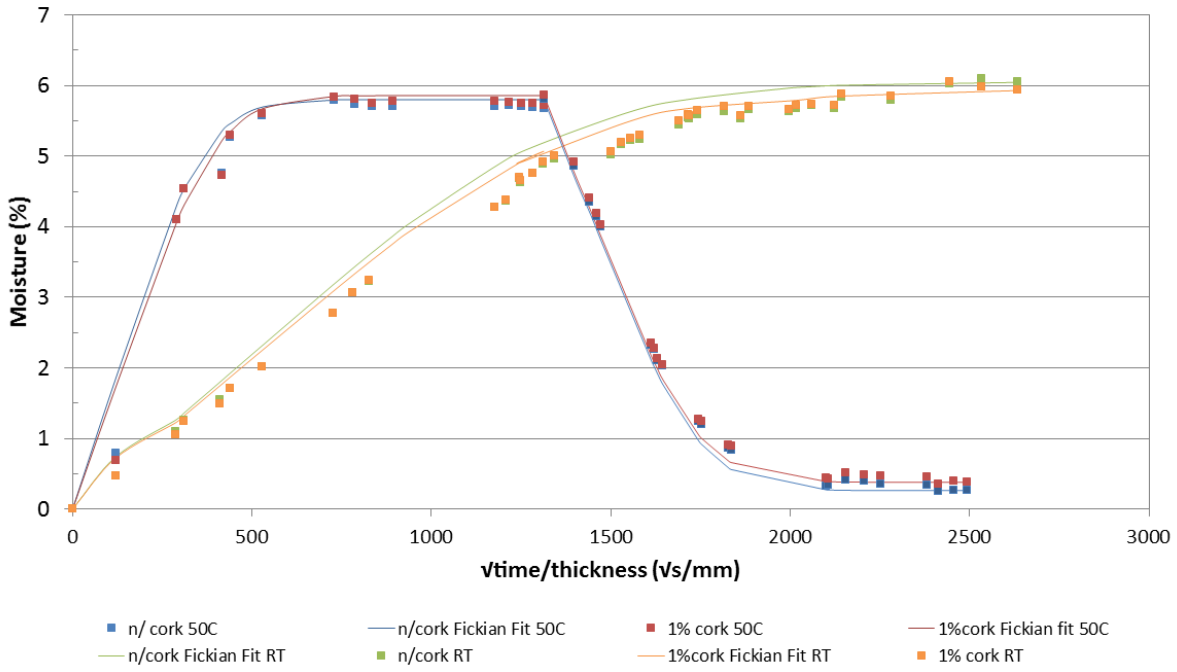

Figure 1 –Moisture absorption and desorption for 50°C and RT of neat resin and resin with 1% cork.

Results comparing the relative volume increase ($\Delta V/V_0$) for specimens with and without cork due to swelling, at different aging temperatures, are presented in Table 1. Analysing the results, we find that the presence of cork does not influence the change in volume. Comparing the values for the absorption and desorption at 50°C, it is observed that the swelling value is approximately the same. Except for the value of desorption of n/cork specimens, but the difference is very slight and can be due to deviations in the measurement. Several authors [19,30-32] reported that the swelling varies with temperature, i.e. the higher the temperature the greater relative change in volume. They also suggested that water molecules can exist in the polymeric network in two states: water molecules filling the free volume of the network or water infiltrating the polymer molecular structure through hydrogen bonding. In the first case, water molecules are relatively mobile within such a free volume. In this case swelling does not occur because water fills volume that already exists. In the second case, water molecules become immobilized and swelling occurs. Thus, there are experiments which show an

increased volume and others do not, it will depend on the nature of the bond between the water and the polymer chain.

In Table 1, there is a slight increase in volume variation with temperature increase, but it is not very significant.

Table 6 - General properties of absorption and desorption.

Stage	Temperature (◦C)	Property	No Cork	1% Cork
Absorption	RT	M∞ (%)	6.05	5.93
		D ($m^2.s^{-1}$)	$1.03*10^{-13}$	$1.01*10^{-13}$
		$\Delta V/V_0$ (%)	1.09±0.03	1.09±0.03
	50	M∞ (%)	5.80	5.86
		D ($m^2.s^{-1}$)	$1.3*10^{-12}$	$1.17*10^{-12}$
		$\Delta V/V_0$ (%)	1.10±0.05	1.10±0.02
Desorption	50	M∞ (%)	5.48	5.53
		D ($m^2.s^{-1}$)	$1.03*10^{-12}$	$1.01*10^{-12}$
		$\Delta V/V_0$ (%)	1.08±0.05	1.10±0.03

3.1.2 – Measurements of the glass transition temperature *(T_g)*

Figure 2 shows the average T_g value of the neat epoxy resin and of the epoxy resin with 1% of cork particles in different stages of moisture (as cast, dry, saturation at RT and 50°C). Barbosa et al. [2,20] in a previous study showed that specimens with cork particles present a lower T_g compared to specimens without cork and it was concluded that the presence of cork was responsible for the increase in toughness.

During the dry process, a post-cure of the adhesive probably occurred, which increased the crosslinking leading to an increase in T_g. For thermosets exposed to temperatures below the T_g for long periods of time (annealing), there is an increase in mass density (volumetric relaxation) and this phenomenon is known as physical ageing, with influence on mechanical of epoxies. Physical ageing in glassy thermosets system, which is the case of Araldite 2020®, has been associated with increases in density, T_g, modulus and yield stress, and also decreased free volume. In addition to the crosslinking increase, the samples also lose the existing water, inherent in the manufacturing process, this also leads to the T_g increase. [37]. Thus the drying process to which the samples are subjected can lead to the increase of Tg. In addition to the crosslinking increase, the samples also

lose the existing water, inherent in the manufacturing process, this also leads to the Tg increase.

As moisture diffuses into the epoxy resin, it affects the chain mobility of the polymer. These changes in the molecular chain causes inevitable changes in T_g [38], with an usual decrease in the T_g value [30,39].

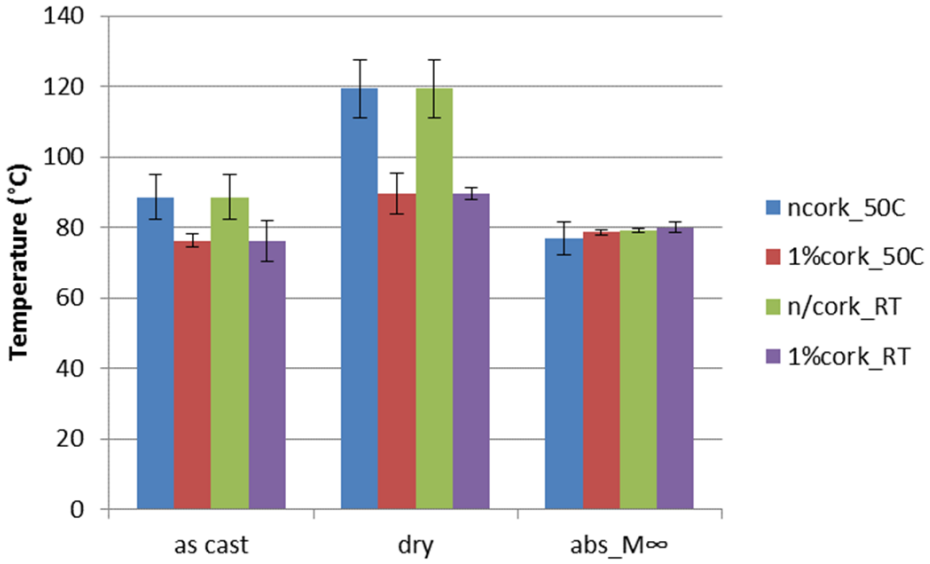

Figure 2 - Glass transition temperature of specimens with different moisture stages (as cast, dry and moisture saturation at RT and 50°C) for different amounts of cork (neat resin and with 1% of cork).

3.1.3 – Tensile tests

In order to investigate the influence of moisture and temperature, tensile tests were performed at RT in specimens as cast, dry and moisture saturated. Figure 3 shows typical tensile stress-strain curves of the neat epoxy resin and of the epoxy resin with 1% of cork particles in different stages of moisture (as cast, dry, and M_∞ at absorption at RT and 50°C). The effects of hygrothermal aging on the tensile strength, maximum strain and Young's modulus of the studied epoxy system are shown in Figures 4, 5 and 6 respectively.

In the as cast stage, it is observed that the presence of cork favours the adhesive ductility. Specimens with 1% of cork present a higher maximum strain to failure than specimens without cork particles. This fact has been previously studied by the authors

[2,20]. However when the pieces are dry, it is observed that the adhesive becomes more fragile, the maximum tensile stress and Young´s modulus increase, both for the neat epoxy resin and for the epoxy resin with 1% cork (see Figures 3, 4, 5 and 6). What probably happens is that increasing the temperature to 50°C leads to a post-curing of the adhesive and hence a change in its mechanical properties. However, this step is required since it ensures that when the sample is immersed in water, there are no water molecules in the polymer chain. These water molecules are derived from manufacturing processes and/or the environment humidity.

Changes in mechanical properties are also observed with the immersion of specimens in water, regardless of the temperature (RT and 50°C). The temperature promotes the moisture diffusion and in both specimens there is a degradation of properties. Moreover, the colour of the specimens changed from colourless to yellow.

Specimens remained immersed in water until they reached water saturation and were immediately tested after that. With the incorporation of water molecules in the polymer network, the displacement increases. However it is most notorious for samples which were immersed in water at 50°C (see Figure 3). With the increase of water temperature, the maximum tensile stress and maximum strain increase in relation to specimens immersed at RT, however, the Young's modulus decreases (see Figure 4, 5 and 6). This result is in accordance with several studies [33-35] showing that hydrothermal aging affects mechanical properties, decreasing the tensile strength and Young´s modulus of the epoxy resin.

The amount of cork present in the adhesive also influences the properties of the material when immersed in water. Specimens with n/cork present a higher maximum strain and a higher Young's modulus, compared to specimens with cork, when they reach the moisture saturation (see Figures 5 and 6). Figure 4 shows the maximum strength results. Specimens which had absorption at RT present a higher maximum strength compared to specimens which had the same procedure at 50°C. Analysing this figure it can also be concluded that the presence of cork does not have influence because specimens with and without cork present similar results for both temperatures (RT and 50°C).

The tensile test results T_g values obtained are in line with the, i.e. an increase of the strain corresponds to a decrease in the T_g value.

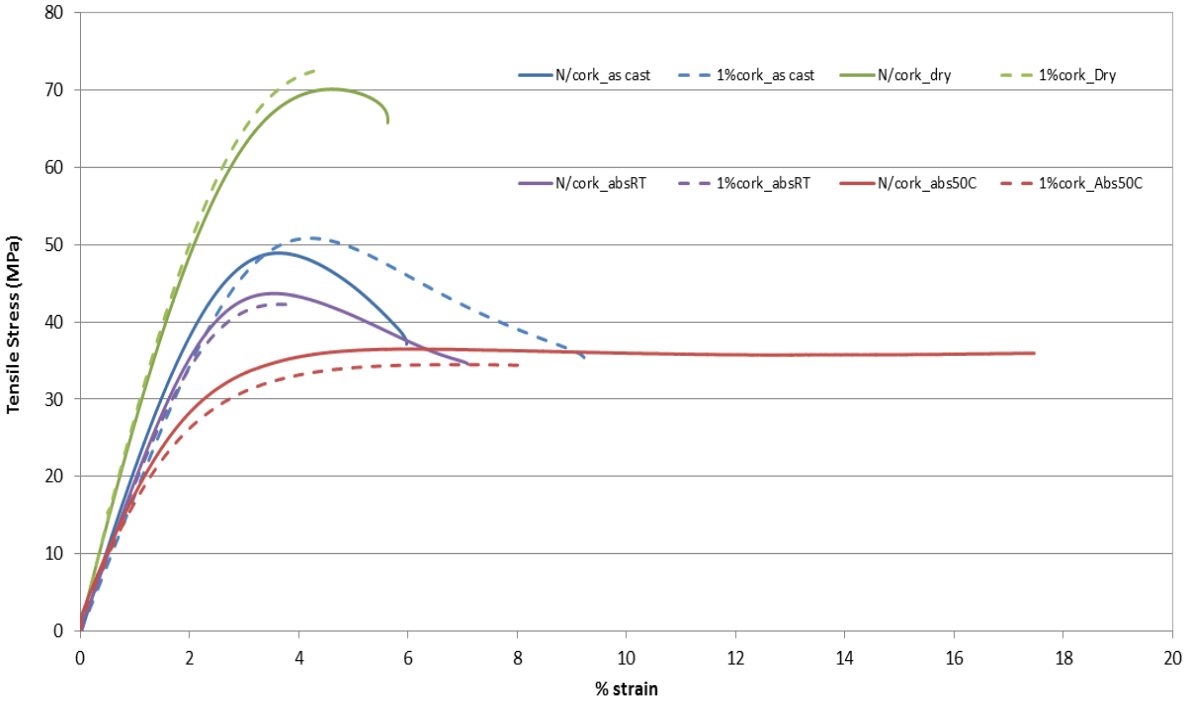

Figure 3 – Tensile stress-strain curves of specimens with different moisture stages (as cast, dry and moisture saturation at RT and 50°C) for different amounts of cork (neat resin and with 1% of cork).

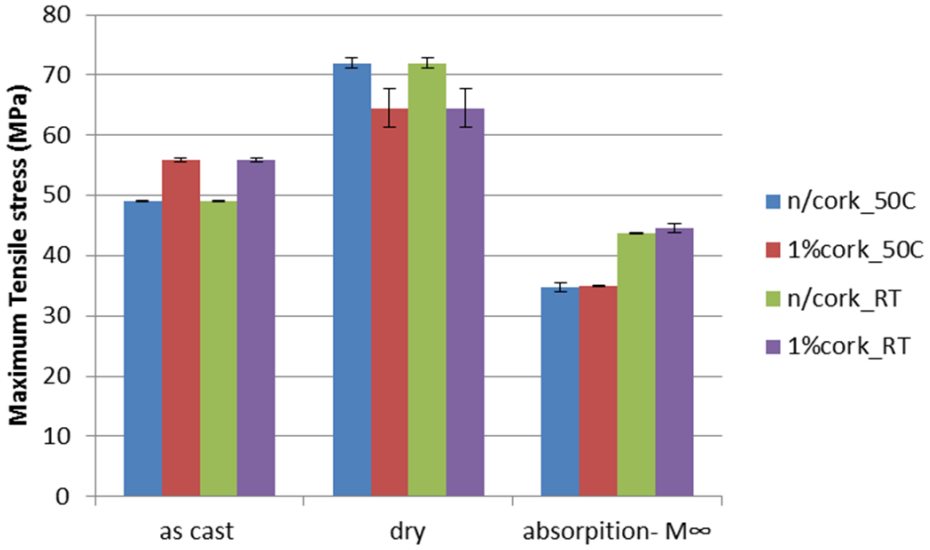

Figure 4 - Maximum tensile stress of specimens with different moisture stages (as cast, dry and moisture saturation at RT and 50°C) for different amounts of cork (neat resin and with 1% of cork).

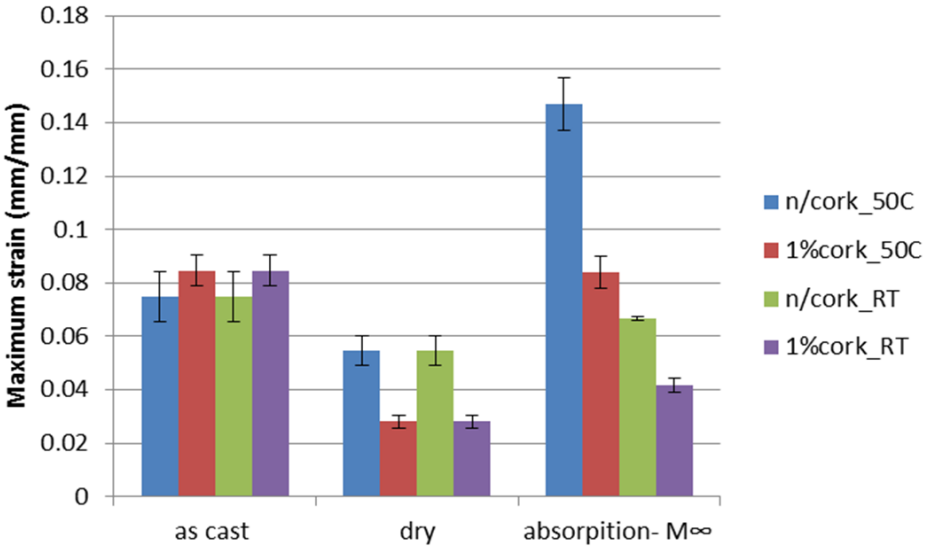

Figure 5 - Maximum strain of specimens with different moisture stages (as cast, dry and moisture saturation at RT and 50°C) for different amounts of cork (neat resin and with 1% of cork).

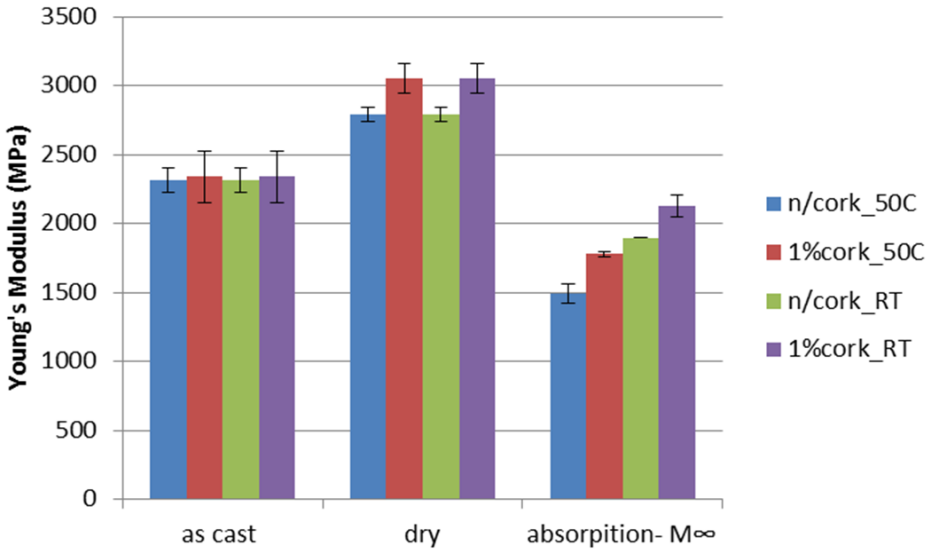

Figure 6 – Young's Modulus of specimens with different moisture stages (as cast, dry and moisture saturation at RT and 50°C) for different amounts of cork (neat resin and with 1% of cork).

3.1.4 – SEM of the fracture surface of tensile test specimens

With the aim of understanding the hygrothermal aging effect on fracture mechanisms, fractographic studies of the tensile specimens fracture surface were performed using SEM. Figure 7 presents the fracture surface of the tensile specimens for different stages of moisture absorption (as cast, dry, saturation at RT and 50°C). Araldite 2020® is a very brittle epoxy and its fracture presents one slow crack zone at the beginning of the crack growth and one rapid crack growth zone when the instability criterion for crack growth is met with the continually increased loading. The slow crack zone is near the crack initiation point and rapid crack growth is away from the crack initiation point. Analysing the images of the neat epoxy resin and the epoxy resin with 1% cork in the as cast condition, considerable differences can be observed. This issue has already been analysed in previous studies, which concluded that specimens with 1% cork present a more ductile behaviour compared to the neat epoxy resin sample [2,20]. The neat epoxy resin presents a relatively smooth fracture surface in the slow crack growth zone. Away from this area, there are spaced “rib” markings perpendicular to the direction of crack growth in the crack speeding zones. For specimens with 1% cork the smoothness in the slow growth of the fracture zone is not as noticeable; the fracture is more ductile. With the drying of the specimens there is probably an increase in crosslinking, as mentioned earlier. The increased mechanical strength of the material is manifested in the fracture surface, with a more brittle fracture (see Figure 7 - dry). With water saturation (at RT and 50°C), clear differences in the mechanical behaviour of the specimens were observed; the maximum tensile stress decreases and the maximum strain increases substantially for specimens of neat epoxy resin. For specimens with 1% of cork there is no major difference in the maximum strain value. An increase in the value of the strain is usually associated to fracture with a ductile appearance, which does not occur in this case. For both cases the fracture suggests a brittle failure, with a larger rapid crack growth zone.

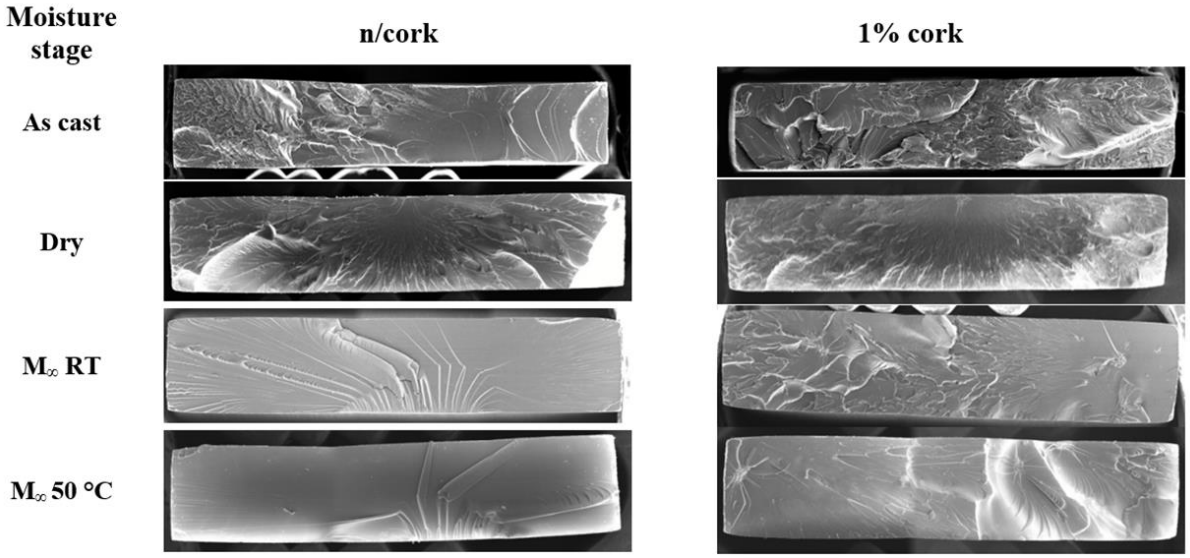

Figure 7 - Fracture surface of tensile specimens for different moisture absorption stages.

In the case of materials reinforced with natural fibres, in addition to the degradation of the polymeric material, there is also frequent degradation of the natural fibres. Some studies [36] show that degradation of the mechanical properties of natural fibre reinforced composites is larger than that of synthetic fibre reinforced composites. This fact is due to the higher moisture sorption behaviour and the organic nature of the natural fibre. Figure 8 shows the cork particles in different states: before inclusion in the epoxy resin; after inclusion in the epoxy resin in the as cast condition, and included in the epoxy resin after moisture saturation. It can be observed clearly that, contrary to what typically occurs in natural fibres, the cork does not degrade in contact with moisture.

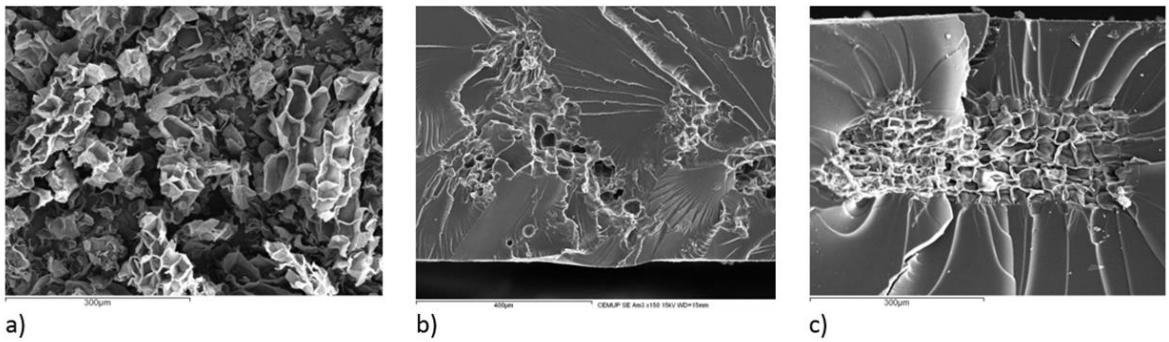

Figure 8 – Cork particles (125-250 µm): a) cork particles before inclusion in the resin; b) Epoxy resin with cork particles as cast; c) Epoxy resin with cork particles, after moisture saturation.

3.2 – Absorption plus desorption

After hydrothermal aging (until moisture saturation), the specimens were dried in order to evaluate the influence of desorption on the chemical and mechanical properties. The drying process during desorption was performed at 50°C. It was decided not to perform desorption tests at RT because at this temperature the study would take too much time.

3.2.1 Tensile tests

Figure 9 shows typical tensile stress-strain curves of the neat epoxy resin and of the epoxy resin with 1% of cork particles in different stages of moisture (cast, dry, M_∞ at absorption and desorption). The effects of hygrothermal aging on the tensile strength, maximum strain and Young's modulus of the studied epoxy system are shown in Figures 10, 11 and 12 respectively.

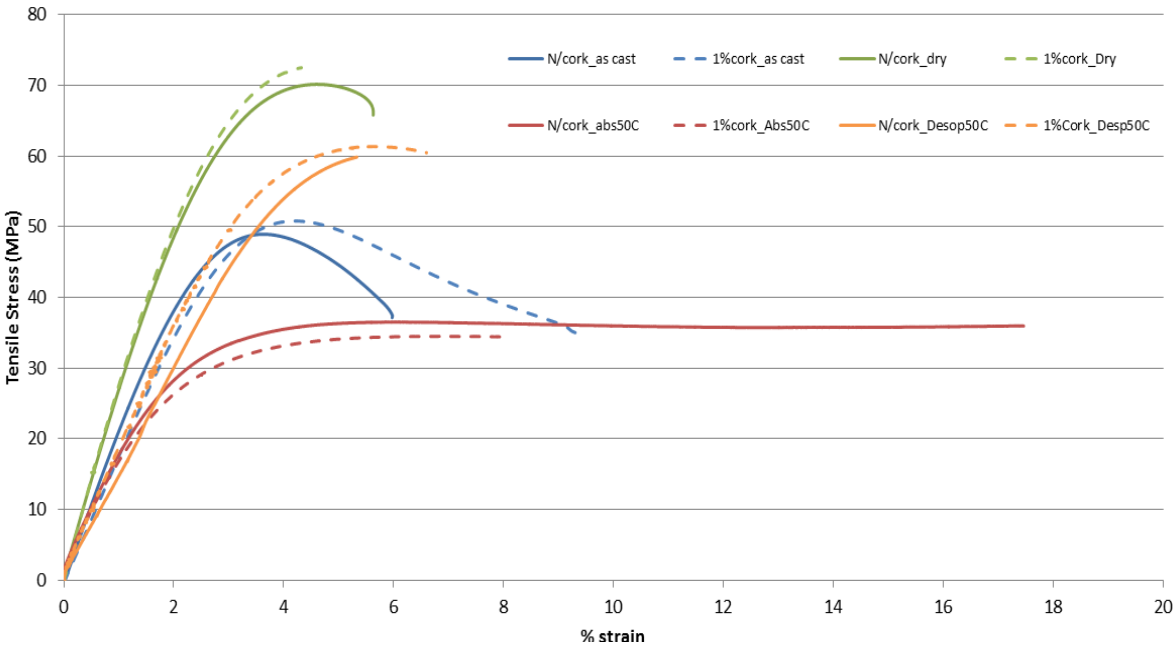

Figure 9 - Tensile stress-strain curves of specimens with different moisture stages (as cast, dry, M_∞ absorption and at M_∞ desorption) for different amounts of cork (neat resin and with 1% of cork).

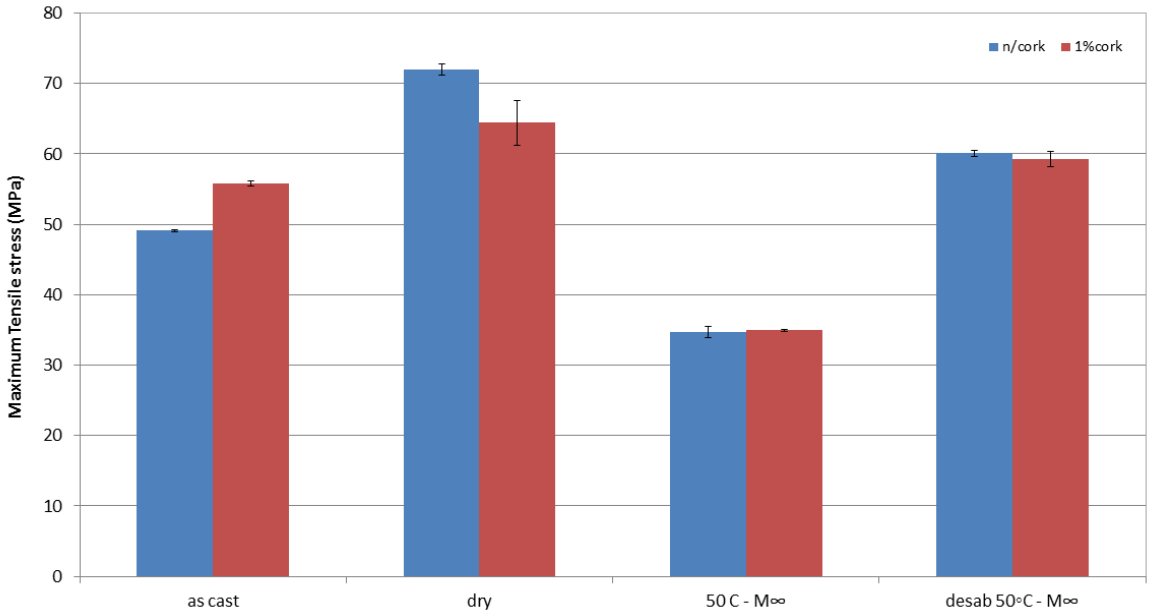

Figure 10 - Maximum tensile stress of specimens with different moisture stages (as cast, dry, M_∞ absorption and at M_∞ desorption) for different amounts of cork (neat resin and with 1% of cork).

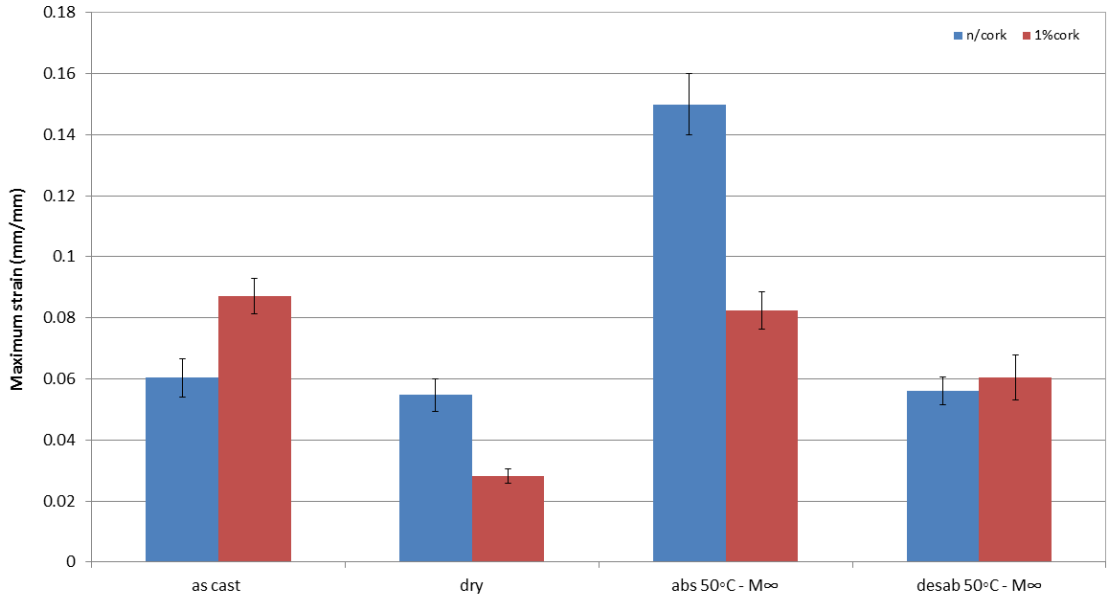

Figure 11 - Maximum strain of specimens with different moisture stages (as cast, dry, M_∞ absorption and at M_∞ desorption) for different amounts of cork (neat resin and with 1% of cork).

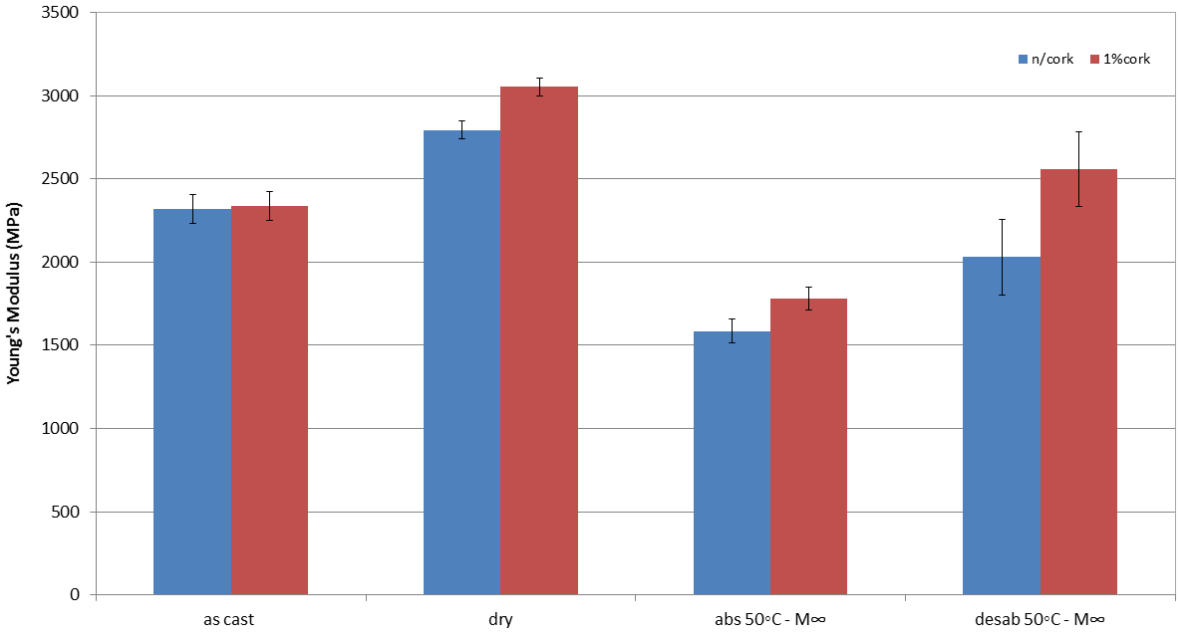

Figure 12 – Young's modulus of specimens with different moisture stages (as cast, dry, M_∞ absorption and at M_∞ desorption) for different amounts of cork (neat resin and with 1% of cork).

Analysing Figures 9 - 12, it can be clearly observed that the hydrothermal cycles significantly alter the mechanical properties of the epoxy. The drying process might have led to an increase in crosslinking, causing a change in the properties. Subsequently to

the absorption of water, there was a distension of the molecular chains. Finally, during the process of desorption of water, there was probably the creation of voids in the molecular chain (formerly occupied by water molecules). All these factors lead to changes in the mechanical properties.

Comparing the results obtained between the neat epoxy resin and the epoxy resin modified with cork it can be observed that they behave differently. When water is absorbed, the neat epoxy resin has a higher deformation capacity (compared with the composite). In contrast, after the desorption process, the materials have behaviour similar to the as cast. In both conditions, the composite always presents a Young's modulus higher than that of the neat epoxy resin. It is concluded that the epoxy resin without the cork is more susceptible to hydrothermal degradation. This should be most likely because water does not have as much capacity to broaden the molecular structure due to the impediment of cork particles.

Figure 13 shows the fracture surfaces after absorption and desorption of moisture. At first sight, these fracture surfaces present conflicting results compared with the results of the tensile test since flat fracture surfaces generally corresponds to a brittle fracture, typically associated with a smaller displacement of the specimen. As mentioned previously, the samples of moisture absorption actually suffer a fairly brittle failure despite having more displacement. It is observed that the brittle fracture in absorption specimens becomes a more ductile surface, similar to that obtained in the cast state.

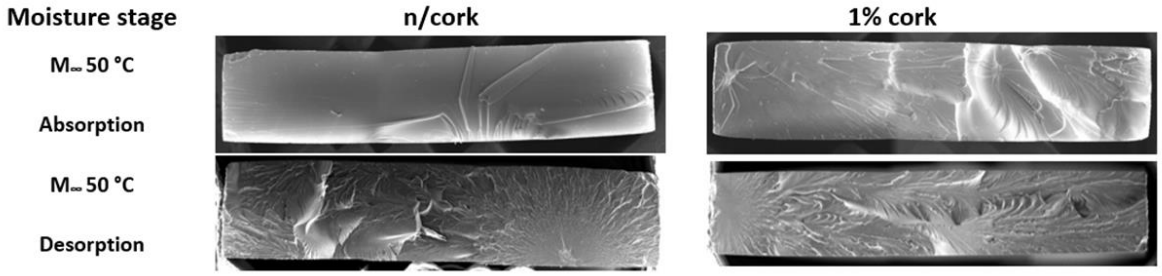

Figure 13 - Fracture surface of tensile specimens for different moisture stages (absorption and desorption) at 50 °C.

3.2.2 – Measurements of the glass transition temperature (T_g)

Figure 14 shows the average T_g value of the neat epoxy resin and of the epoxy resin with 1% of cork particles at different stages of moisture (as cast, dry, $M\infty$ absorption and at $M\infty$ desorption). A change was observed in the tensile properties of the material, and this is also reflected in T_g. The values of T_g are very close to those obtained initially, demonstrating no permanent damage in the epoxy.

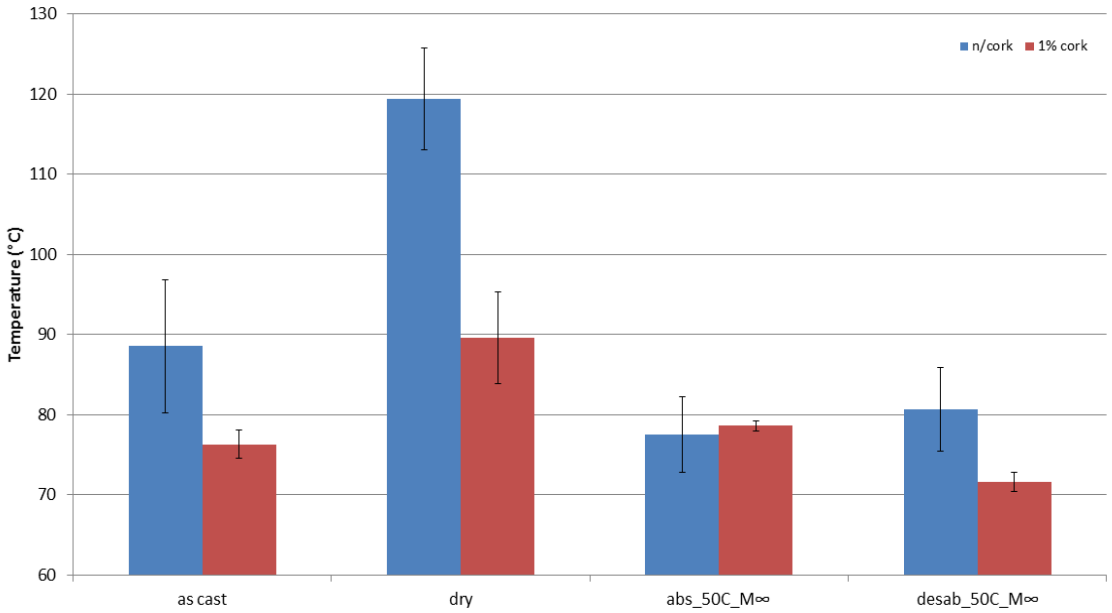

Figure 14 - Glass transition temperature of specimens with different moisture stages (as cast, dry, M_∞ absorption and at M_∞ desorption) for different amounts of cork (neat resin and with 1% of cork).

3.3 – Fourier transform infrared spectroscopy (FTIR)

The previous results demonstrated that the presence of water can alter the properties of the materials studied. It was also observed that there were differences in the mechanical behavior in specimens with and without cork. It is necessary to analyze whether these differences are also visible at the level of the chemical structure. For this purpose, the unaged and aged epoxy resin was analyzed by FTIR.

Figure 15 show the spectrum in the 4000-450 cm^{-1} wavenumber range of Araldite 2020®, neat epoxy resin and with 1% cork, respectively. This figure show the four states of moisture studied in this research: as cast, dry, absorption and desorption at 50 °C.

A general analysis of the data in Figure 15 leads to the conclusion that the spectra are quite similar, indicating that no major changes in the chemical structure of the adhesive occur due to the addition of cork.

Exploring the spectrum as cast and dry for the neat epoxy resin (Figure 15), some differences can be observed. The –OH $–CH_2$ and C-N group decreases due to the drying of the specimen. The epoxy ether group increases probably due to post-curing of the specimen.

After hygrothermal aging, there is an increase of the –OH, as this absorption is due to O-H and N-H stretching and intermolecular hydrogen bonds; this can be explained by the fact that water absorption induces hydroxyl and amine groups into the epoxy chain. It is also observed that C-H stretching vibrations (3100-2800 cm^{-1}) increase, which arises from aliphatic hydrocarbons, which also changes with the water absorption. Furthermore, changes are observed in C=C streching of the benzene ring (1509 cm^{-1}) and the out-of-plane bending of aromatic rings (830 cm^{-1}). The aromatic band (1246 cm^{-1}) increases when bonded water is present [40,41]. All these changes mentioned show that there is water absorption by the epoxy resin. Analyzing the spectra of Figures 15, it is observed that the -OH peak is higher for samples with 1% of cork. This value is apparently seems inconsistent since analyzing Table 1, these two materials had very similar percentages of absorption. It was observed that there is a small difference in the initial weights of the specimens that were subjected to the absorption test. The specimen with 1% cork is slightly heavier, which is reflected in the amount of absorbed water. Although specimens with and without cork absorb approximately the same amount of water (in percentage) when we analyze the corresponding mass it is observed that there is an increase of 3.75% between samples n/cork and 1%cork. This may explain why the spectrum of the specimens with 1% cork has a larger band of OH.

With the process of water desorption it is observed that the spectrum is very similar to the initial state. The peaks of oxirane and benzene rings remain without significant changes, which lead to the conclusion that there is no permanent degradation of the epoxy resin. The spectra of the epoxy resin with 1% cork (Figure 15) is very similar to n/cork spectra, although some differences exist primarily in the –OH, $-CH_2$, $-CH_3$ and C-N group.

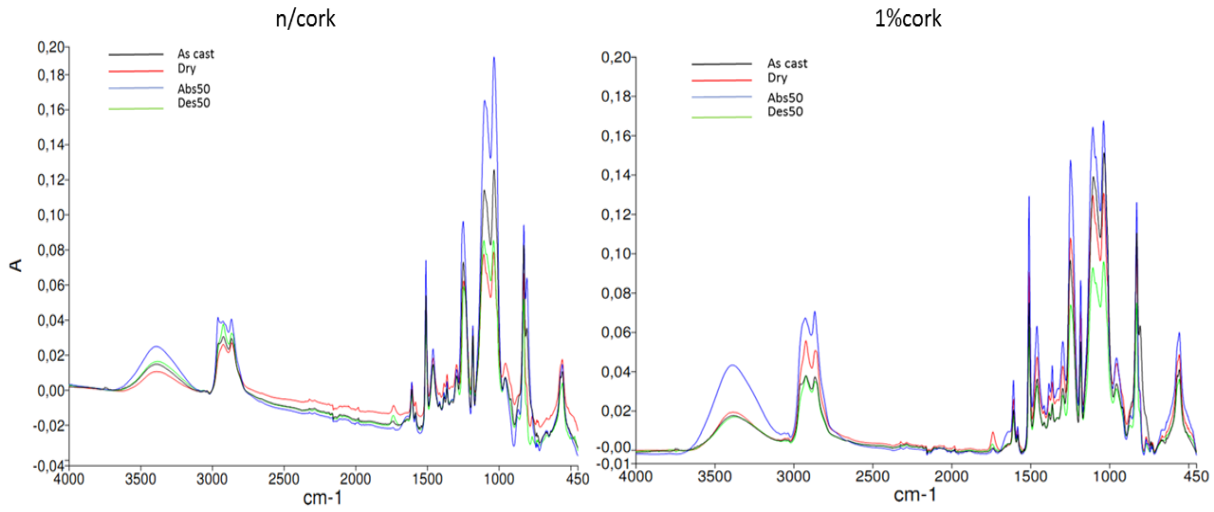

Figure 15 - FTIR spectrum, in the 4000–450 cm-1 wavenumber range of neat resin and epoxy resin with 1%, for different stages of moisture (as cast, dry, M_∞ absorption and at M_∞ desorption).

4 - CONCLUSIONS

The hygrothermal aging of an adhesive reinforced with micro particles of cork was evaluated by diffusion tests, tensile strength, analysis of surface fracture, T_g measurements and FTIR analisys. The tests were performed on specimens with neat epoxy resin and epoxy resin with 1% of cork. The following conclusions can be drawn:

- Both materials have very similar diffusion rates, which means that the presence of cork does not have a great influence on the absorption / desorption of moisture. The temperature influences the rate of diffusion, i.e. the increase of temperature increase the diffusion rate;

- With the moisture uptake, it is observed that there is a deterioration of the mechanical properties, particularly for specimens subjected to higher temperatures. The neat epoxy resin samples show a greater variation in mechanical properties, compared with the samples containing 1% of cork;

- Contrary to what typically occurs in the natural fibres used to reinforce polymers, the cork does not degrade in contact with moisture, since cork is rootless;

- The analysis of the functional groups present in both types of samples shows that there are changes (especially in the -OH group) along the various states of humidity. Nevertheless after drying, the samples show very similar values to those present in the initial state.

ACKNOWLEDGEMENTS

Financial support by Foundation for Science and Technology (PTDC/EME-TME/098752/2008 and SFRH / BD / 88173 / 2012) are greatly acknowledged. The authors want to thanks also to Edilene Neve and Lucas Chetto, from the Ciência Sem Fronteiras project, throughout the help provided in the course of this investigation.

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